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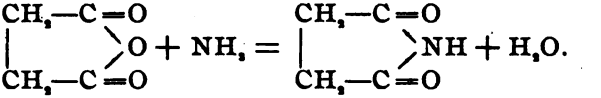
SUCCINIMID.

BY EDMUND H. MILLER.

PART I.

Received April 12, 1894.

SUCCINIMID was discovered in the year 1835 by Felix d' Arcet,[1] who prepared it by acting on succinic anhydride with ammonia gas, according to the reaction.



He noticed that when the two bodies were allowed to react, there was a great elevation of temperature, that a considerable amount of water was evolved, and that a compound much more fusible than succinic acid resulted; by aiding the reaction with heat, a white substance was sublimed which had none of the properties of succinic acid.

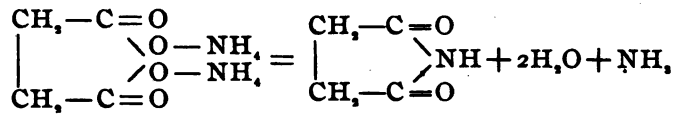
D' Arcet found that this substance which he called succinamid, crystallized in regular rhombs from ether and alcohol and contained one molecule of water when crystallized from that solvent, also it gave off ammonia when treated with hot caustic potash. He considered the formula as $C_4H_5NO_2$ from his analysis which would correspond to $C_4H_6NO_2$, according to the atomic weights now in use.

Bisuccinimid. This compound is identical with that prepared by D' Arcet and was so named by Fehling[2] who prepared it by conducting dry ammonia-gas over melted succinic acid, and recrystallizing the sublimate. He announced the melting point to be 210° C. Fehling also prepared this compound by

[1] *Ann. chim. phys.*, [2] 58, 282–300, *1835*.

[2] *Ann. Chem.*, (Liebig), 49, 98, *1844*.

neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and then distilling; ammonia and water go off first and then bisuccinimid and a little succinic acid are sublimed.



Bisuccinimid was also obtained similarly from acid ammonium succinate by the splitting off of water.

Fehling found that an aqueous solution of bisuccinimid dissolved lead oxide in great quantities giving the lead salt containing fifty-eight per cent. of lead. He also announced that barium gave a similar compound.

The name succinimid was given to the compound by Laurent and Gerhardt[1] who devoted considerable time to its investigation, and first prepared the silver salt.

Trisuccinimid was prepared by Gerhardt and Chiozza[2] by the action of succinyl chloride on silver succinimid as follows: $C_2H_4(CO)_2Cl_2 + 2AgN(CO)_2C_2H_4 = N_2(C_4H_4O_2)_2 + 2AgCl$.

Teuchert,[3] in his experiments on succinamic acid, gives the following statements concerning succinimid:

1. By treating succinimid with barium hydroxide the barium salt of succinamic acid is obtained.

2. On decomposing salts of succinamic acid by acids with the aid of heat, ammonium succinate is formed, not succinimid, as stated by Laurent and Gerhardt.

3. The compound called silver succinamate by Laurent and Gerhardt must not be considered as this compound, but as a silver hydroxide succinimid.

Teuchert also prepared the potassium, magnesium, manganese, cadmium, zinc, and copper salts of succinimid.

In 1869 Erlenmeyer[4] redetermined the melting point of succinimid and found that instead of being 210° as stated by both Fehling and Teuchert, it was 125°–126°. Erlenmeyer denied the

[1] *Compt. rend.*, *1847*, 291, and *1849*, 108.
[2] *Ann. Chem.*, (Liebig), 134, 136, *1865*.
[3] *Ann. Chem.*, (Liebig), 134, 136, *1865*.
[4] *Ztschr. fur Chemie*, 12, 174, *1869*.

conjecture made by Mendelejeff that succinimid might be identical with the isomeric compound, cyanpropionic acid on account of its formation from succinic anhydride, and from succinamid by the decomposition of two NH_2 groups into NH and NH_3: he ascribed its acid properties to the fact that the hydrogen is combined with a nitrogen attached to the rest of the molecule by two CO groups, and further states that it is an imid, and, therefore, plays the part of a monobasic acid.

Bunge,[1] in 1870, confirmed the melting point of succinimid obtained by Erlenmeyer; he found that it crystallized free from water when acetone was used as a solvent and obtained rhombic octahedra, whose axes were as follows: brachydiag.: makrodiag.: vertic. $a : b : c = 0.7888 : 1 : 1.3655$.

Bunge first replaced the hydrogen of the NH group by a nonmetallic element when he formed iodine succinimid by treating silver succinimid with iodine dissolved in acetone or ether. The iodine succinimid reacted with silver nitrate and formed succinimid again. Menshutkin,[2] in 1872, found that there existed two silver compounds with succinimid, one containing no water of crystallization and the other one-half a molecule. He also states that the hydrogen of the NH group can be replaced by mercury, but that the lead, barium or calcium oxides convert it into the corresponding salt of succinamic acid, thus confirming Teuchert's results.

Succinimid may be converted into the amide by alcoholic ammonia at the temperature of the room, or more quickly by heating them together in a sealed tube at 100° C.

Menshutkin prepared succinimid by distilling succinic acid with acetamide. $C_4H_6O_4 + C_2H_5ONH_2 = C_4H_4O_2NH + C_2H_4O_2 + H_2O$.

He also gave the following definition of an imid: "The imid is that acid amide, which, by the taking up of water, gives the amic acid, and by absorption of ammonia gives the amide." To Menshutkin[3] belongs the distinction of first preparing an organic compound of succinimid; he accomplished this by distilling succinic acid and ethylamine and also by their solution in

[1] *Ann. Chem.*, (Liebig), Suppl., 7, 118, *1870*.
[2] *Ann. Chem.*, (Liebig), 162, 166, *1872*.
[3] *Ann. Chem.*, (Liebig), 182, 90, *1876*.

the proper proportions. Ethyl succinimid melts at 26° and boils at 234°, has a vapor density of 4.61 (compared to air) and is easily soluble in water, alcohol or ether. It is entirely decomposed into ethylamine and succinic acid by treating with caustic potash, and by gentle warming with barium hydroxide, gives the characteristic conversion into ethyl succinamic acid. Methyl succinimid, was similarly prepared.

The first evidence of the symmetrical formula of succinimid is found in the statement of Bell[1] that succinimid by distillation with zinc dust, or on reducing its vapor by hydrogen, yields pyrrol; the presence of pyrrol is shown by the reaction with pine moistened with hydrochloric acid.

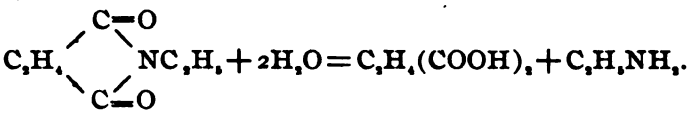
This fact is confirmed by Bernthsen[2] who repeated the experiments, and who also investigated the action of phosphorus trichloride on succinimid, and announced that it gave a fluid chloride. Erlenmeyer's statement that succinimid was not identical with cyanpropionic acid was confirmed in 1882 by Landsberg[3] who, besides preparing a number of metallic salts of succinimid, found that ethyl succinimid when decomposed gave ethylamine and not ethyl alcohol. (This fact was first observed by Menshutkin, but he drew no conclusions from it.) Landsberg made the following statement of the matter:

If succinimid is $C_2H_4\begin{matrix}-CN\\-COOH\end{matrix}$ then the ethyl ester is $C_2H_4\begin{matrix}-CN\\-COOC_2H_5\end{matrix}$; this body by treatment with either bases or acids would give

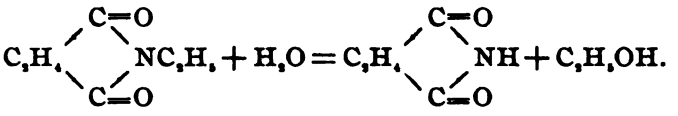
$$\begin{matrix}CH_2-CN\\ |\\ CH_2COOC_2H_5\end{matrix} + 3H_2O = \begin{matrix}CH_2COOH\\ |\\ CH_2COOH\end{matrix} + NH_3 + CH_3OH.$$

But if succinimid is $C_2H_4\begin{matrix}C=O\\ \diagdown\ \diagup\\ NH\\ \diagup\ \diagdown\\ C=O\end{matrix}$ the ethyl ester is $C_2H_4\begin{matrix}C=O\\ \diagdown\ \diagup\\ NC_2H_5\\ \diagup\ \diagdown\\ C=O\end{matrix}$ and such a body would give

[1] *Ber. d. chem. Ges.*, 13, 877, *1880.*
[2] *Ber. d. chem. Ges.*, 13, 1047, *1880.*
[3] *Ann. Chem.*, (Liebig), 215, 172, *1882.*

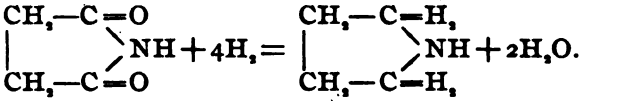


The fact that Menshutkin obtained succinimid and alcohol when he treated silver succinimid with ethyl iodide instead of ethyl succinimid and silver iodide, is explained by the water of crystallization present in some silver succinimid which decomposes the ethyl ester of succinimid first formed as follows:



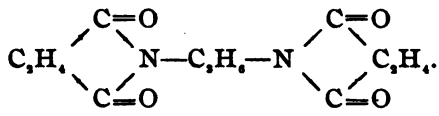
Cimian and Silber[1] investigated the action of bromine on succinimid. They found that the hydrogen of the imid group was not attacked but that when a calculated amount of bromine was dropped i nto a flask containing succinimid heated to 160° C., that hydrobromic acid was given off, and bibrommaleicimid $(CBr)_2(CO)_2NH$ was formed (M. P. 225° C). This imid when treated with aqueous caustic potash gave bibrommaleic acid. The corresponding anhydride, and the barium and silver results were also made. Bender[2] treated succinimid with calcium chloride in acetic-acid solution and obtained chlorine succinimid $C_2H_4(CO)_2NCl$, which crystallizes in large colorless crystals from boiling benzene, melts at 148° C. without decomposition, and by treatment with hydrochloric acid or alkalies forms succinimid again.

Ladenburg[3] found that by reducing succinimid by sodium, in an alcoholic solution, he obtained pyrrolidin.



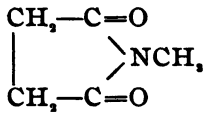
A curious body was made by Strache[4] by heating together two molecules of succinic anhydride and one of propylene diamine, called propylene succinimid. Its melting point is 98°–100° C. and has the formula

[1] *Ber. d. chem. Ges.*, 17, 556, *1884*.
[2] *Ber. d. chem. Ges.*, 19, 2273, *1886*.
[3] *Ber. d. chem. Ges.*, 20, 215, *1887*.
[4] *Ber. d. chem. Ges.*, 21, 2360, *1888*.

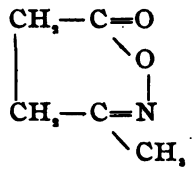


A most extraordinary method of making methyl succinimid was announced by Bredt and Boeddinghous[1] in 1889. They found that the valeroximidolacton of Rischbieth, which is made by treating isonitrosovalerianic acid (made from levulinic acid and hydroxylamine) with concentrated sulphuric acid, to be identical with methyl succinimid, both in melting and boiling points and to give succinic acid and methylamine on treatment with caustic potash.

Methyl Succinimid.



γvaleroximidolacton.



The only conclusions that can be drawn from this remarkable reaction are that either the formula given above for methyl succinimid is wrong or, as is more probable, that the compound must undergo an elaborate molecular rearrangement.

The substitution of a bromine in one of the CH_2 groups of succinimid, was accomplished by Kusserow[2] in 1889. He formed bromsuccinimid $C_2H_3Br(CO)_2NH$ by heating water-free succinimid and bromine dissolved in chloroform in a sealed tube at 120°–130° C. After heating for two or three hours the bromine disappears and the substitution product is seen as a brown oil under the chloroform. $C_2H_4(CO)_2NH + 2Br = C_2H_3Br(CO)_2NH + HBr$.

If water is present and the tube is heated to 160° a mass of white crystals results and scarcely any pressure. The bromsuccinimid is attacked by the hydrobromic acid and water as follows:

$C_2H_3Br(CO)_2NH + 2H_2O + HBr = C_2H_3Br(COOH)_2 + NH_4Br$.

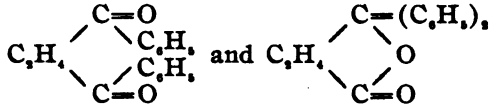
Anilidosuccinimid, $C_2H_3(NH\ C_6H_5)(CO)_2NH$, is formed by warming monobromsuccinimid with an excess of anilin on the

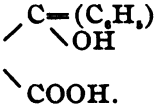
[1] *Ann. Chem.*, (Liebig), 251, 316, *1889*.
[2] *Ann. Chem.*, (Liebig), 252, 158, *1889*.

water-bath; from this the following compounds have been made: nitrosoanilidosuccinimid $C_2H_3(N{-}NOC_6H_5)(CO)_2NH$ and acetylanilidosuccinimid $C_2H_3(NC_2H_3OC_6H_5)(CO)_2NH$.

Anilido succinanil $C_2H_3(NHC_6H_5)(CO)_2NC_6H_5$ is formed by warming monobromsuccinic acid with an excess of anilin and recrystallizing the product from alcohol. The corresponding nitroso-compound and the amic acid have also been prepared.

The only investigation pointing towards the existence of an unsymmetrical as well as a symmetrical succinimid is that of Auger.[1] He succeeded in preparing two succinimids by the reaction of ammonia on succinyl chloride in the proportion of eight of the unsymmetrical to one hundred of the symmetrical. He also formed the silver salt corresponding to the silver salt of symmetrical succinimid, but failed to make the unsymmetrical succinimid. Auger's investigation on the imid is very imcomplete so that to draw any inference as to the molecular arrangement of succinimid, we must consider his work on succinyl chloride and phtalimid. Succinyl chloride when acted on by benzene and aluminum chloride in the cold for five hours, gives a mixture of a symmetrical and unsymmetrical compound.

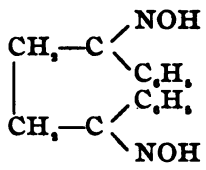


The unsymmetrical compound melts at 90° C., is insoluble in water and cold alkalies, and has a neutral reaction. When treated with potash on the water-bath and then made acid with hydrochloric acid γdiphenyloxbutyric acid separated out, 

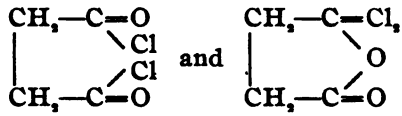
as we would expect from the lactone formula, this body melts at 145° and gives water and the unsymmetrical lactone, M. P. 90° C.

The symmetrical body, separated from the unsymmetrical by fractional distillation, is formed in much smaller quantity. It melts at 134° C. and is unacted on by alkalies. Its symmetrical constitution is shown by the formation of a dioxime.

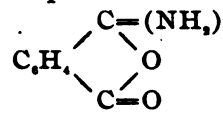
[1] *Ann. chim. phys.*, [6] 22, 289-368, *1891*.



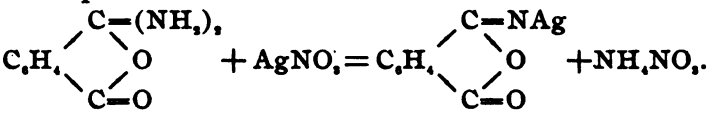
These results show that succinyl chloride is a mixture of the symmetrical and the unsymmetrical.

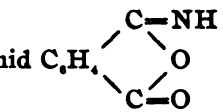


If there are two succinyl chlorides, it would seem that there should be two succinimids and the probability of the existence of the unsymmetrical, at present unknown, is more evident by Auger's research on the amids of phtalic acid.

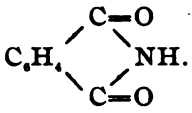
Unsymmetrical phtalamid  is formed by dropping phtalyl chloride into a large excess of aqueous ammonia, then evaporating, drying, and extracting with ninety-nine per cent. alcohol and recrystallizing. It begins to melt at 90° C. and is soluble in water while the symmetrical phtalamid is not.

The unsymmetrical compound gives a silver salt having the composition $C_8H_4O_2NAg$ which is the silver salt of the unsymmetrical phtalimid.



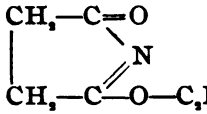
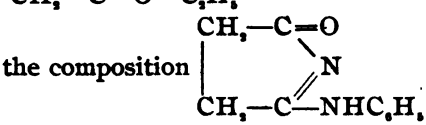
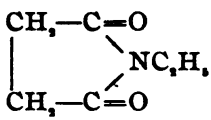
The unsymmetrical phtalimid  is made as follows: To a seven per cent. aqueous solution of the unsymmetrical phtalamid add, in the cold, a quantity of hydrochloric acid calculated to remove one NH_3. A voluminous white precipitate is the immediate result, which, when recrystallized from ninety-five per cent. alcohol, gives a compound which has the same percentage composition as phtalimid, the same appearance,

the same solubility in water, the same acid reaction, and if heated very gently, has the same melting point. But if it is heated rapidly, to about 145° C., it melts, giving a perfectly limpid liquid which in about half a minute, without the disengagement of any gas or vapor, solidifies completely and does not melt till 228° C. is reached, the melting point of the symmetrical phtalimid. It therefore seems that on heating it has undergone a molecular rearrangement and has been converted into the more stable sym-

metrical phtalimid .

The unsymmetrical phtalimid, though similar to the symmetrical in most of its properties, is more easily decomposed by water giving first the amic acid and then the ammonium salt.

The oxygen ethers of succinimid isomeric with the nitrogen ethers previously described, have been prepared recently by Comstock and Wheeler,[1] as follows:

Oxygen ethyl-succinimid. Dry silver succinimid was allowed to stand for several weeks at the ordinary temperature with one molecule of ethyl iodide, diluted with three times its weight of dry chloroform; a dark oily residue was obtained which, when distilled under diminished pressure, gave the ether. It must have the composition  as it gives with anilin a base, having the composition . Some of the nitrogen ether  is formed at the same time, as is proved by allowing the mixture to stand for some time with water, which converts the oxygen ether into succinimid, and then distilling with caustic potash; the distillate showed the presence of primary amine by the isonitril reaction.

[1] *Am. Chem. J.*, 13, 520, *1891*.

The nitrogen ether so obtained agrees in properties with that described by Menshutkin. Oxygen propyl-succinimid was made in the same way, also the isomeric nitrogen ether. The oxygen propyl ether as well as the ethyl ether gives with anilin the base $C_{10}H_{10}N_2O$, melting point 216° C.

Succinimid bromide has been made by Lengfeld and Steiglitz[1] by adding bromine to a solution of succinimid in sodium hydroxide cooled by ice; the yield is ninety to ninety-five per cent. of the theoretical. The melting point is 172.5°; acids instantly liberate bromine and regenerate succinimid; water decomposes it slowly; when pure and dry, it is stable. It is evidently analogous to the succinimid iodide of Bunge, and the succinimid chloride of Bender.

The above compound sometimes called bromyl succinimid was made in the same year by Seliwanow[2] from succinimid and bromyl-acetamide; he gives its melting point as 161°–162° and states that it can also be made from succinimid and hypobromous acid; in the presence of water it acts like hypobromous acid, as does the corresponding chlorine compound. He regards the compound as an amide of hypobromous acid.

It only remains for me to describe here briefly, three new methods by which I have made succinimid.

No. 1. On heating together ethylene cyanide and acetic acid in a sealed tube for eight hours at a temperature of 180°–200° C. the following reaction takes place:

$$C_2H_4(CN)_2 + CH_3COOH = C_2H_4(CO)_2NH + CH_3CN.$$

No. 2. On heating under the same conditions succinic acid and acetonitril, succinimid is formed as follows:

$$C_2H_4(COOH)_2 + CH_3CN = C_2H_4(CO)_2NH + CH_3COOH.$$

No. 3. On heating in the same way equal molecules of succinic acid and ethylene cyanide, two molecules of succinimid are formed, the yield being nearly theoretical.

$$C_2H_4(COOH)_2 + C_2H_4(CN)_2 = 2C_2H_4(CO)_2NH.$$

[1] *Am. Chem. J.*, 15, 215, *1893*.

[2] *Ber. d. chem. Ges.*, 25, 3623, *1892*, and *Ber. d. chem. Ges.*, 26, 423, *1893*.

PART II.

MY EXPERIMENTS ON SUCCINIMID.

First Method. Ethylene Cyanide and Acetic Acid.—Tube No. 1. Three grams of ethylene cyanide (one molecule) were dissolved in 2.25 grams of glacial acetic acid (one molecule) in a small thick glass tube, then a few drops of acetic anhydride were added to render the acid anhydrous; the tube was sealed and heated for two hours at 120°–130° C. and then as no change seemed to have taken place, for six hours at 200° C. On cooling, the tube contained a thick brown liquid.

When this tube was opened several months later, some pressure was observed but no colored flame; the contents were transferred to an evaporating dish and allowed to evaporate slowly. Crystals soon made their appearance, and the entire mass finally turned solid and smelled strongly of acetic acid. To determine a method of purification the solubility of the product was tested as follows:

	Cold.	Hot.
Ether, partially soluble		same
Chloroform, partially soluble		same
Ethyl alcohol, soluble		very soluble
Methyl alcohol, very soluble		very soluble
Benzene, slightly soluble		soluble
Amyl acetate, slightly soluble		same
Carbon disulphide, readily soluble		same
Water, very soluble		same

The mass was dried and extracted with dry ether in a continuous extractor for several hours. On allowing the ether extract to cool, diamond-shaped crystals formed, which were removed and their melting point found to be 123°–124° C. (uncorrected). The ether solution was evaporated to dryness and recrystallized from methyl alcohol, giving white crystals melting at 122.5°–123° C.

These crystals were tested for nitrogen by the prussian-blue reaction, which showed that it was present without doubt. They were also tested with methyl orange in aqueous solution and gave a very light pink, showing that it was neither strongly acid nor alkaline. Comparative tests were made with both cyanacetic acid and succinimid, and the color was found to be almost identical with the latter.

Combustions for carbon, hydrogen and nitrogen were made on some of the best crystals as follows: Nitrogen combustion: weight of substance 0.1211 gram gave 15.15 cc. of nitrogen at a temperature of 23.5°, barometer 769.5 mm.; 14.23 per cent. Carbon and hydrogen determination: weight of substance, 0.1509 gram; weight CO_2, 0.2554; weight H_2O, 0.0760, equivalent to 45.98 per cent. carbon and 5.59 per cent. hydrogen.

As the amount of the recrystallized substance was very small, these combustions could not be checked but some more of the substance had to be prepared as is described later.

Tube No. 2 contained three grams of ethylene cyanide, 4.5 grams of glacial acetic acid and a few drops of acetic anhydride, or one molecule of the cyanide to two of the acid. This tube was treated exactly like No. 1, and the only noticeable difference was that its contents, on evaporation, smelled more strongly of acetic acid, and required longer heating before they solidified, owing to the presence of the greater excess of acetic acid.

The melting point of the crystals from this tube, when purified by crystallization from methyl alcohol, was found to be 123° C. (uncorrected).

A nitrogen determination on crystals from tube No. 2 gave the following figures: Weight substance, 0.2026 gram; volume of nitrogen, 25.5 cc. at 22° C., and 772.5 mm., 14.44 per cent.

The carbon and hydrogen were determined as follows: Weight substance, 0.3303 gram; weight CO_2, 0.5857 gram; weight H_2O, 0.16055 gram, equivalent to carbon 48.36 per cent., and hydrogen 5.39 per cent.

I considered that this substance was identical with that obtained from tube No. 1 and that it was probably succinimid.

The following table shows a comparison of my first results with the calculated percentage of succinimid:

	Tube No. 1.	Tube No. 2.	Succinimid.
C	45.98	48.36	48.48
H	5.59	5.39	5.05
N	14.23	14.44	14.14
M. P.	123°–124° (uncorrected.)	123° (uncorrected.)	124°—125° (according to different authorities.)

As the yield from tube No. 2 was slightly larger than from

tube No. 1, some more of the substance was made for further investigation by using two molecules of acetic acid to one of ethylene cyanide.

Tube No. 3 contained ethylene cyanide, twelve grams, acetic acid, sixteen grams, acetic anhydride, five drops, and was heated for three hours at 170°–180° C. and then for six hours at about 200° C. The appearance of the tube on cooling was the same as Nos. 1 and 2.

Thinking that, if succinimid was produced, acetonitril must also be formed, an endeavor was made to separate by distillation the more volatile contents of the tube before transferring them to an evaporating dish; and by using a paraffin bath, a few cubic centimeters of a liquid which smelled of acetic acid and acetonitril, were obtained.

The contents of tube No. 3, after evaporating, were extracted with dry ether for five hours and yielded twelve grams of good dry crystals (theory, 14.85 grams). A portion of these crystals was purified by crystallization from methyl alcohol and combustions were made on it as follows: Nitrogen determination: Weight substance, 0.1923 gram; volume of nitrogen, 24.6 cc.; temperature, 25° C.; pressure, 771 mm.; 14.34 per cent. nitrogen. Carbon and hydrogen determination: Weight substance, 0.2948 gram; weight CO_2, 0.5264 gram; weight H_2O, 0.1416 gram; 48.69 per cent. carbon; 5.33 per cent. hydrogen.

These figures agree closely with the percentage composition of succinimid, but to confirm them some of the crystals were treated with boiling aqueous caustic potash; ammonia was given off and succinic acid was formed, which was obtained by extracting with ether, and its melting point determined. This agreed with the established melting point of succinic acid. The reactions are as follows:

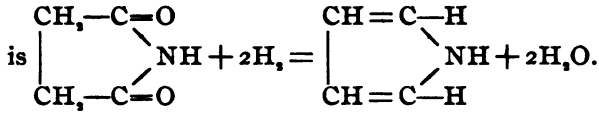
$$\begin{array}{l} CH_2—C{=}O \\ \quad\quad\quad\ \ NH \\ CH_2—C{=}O \end{array} + 2KOH = \begin{array}{l} CH_2—COOK \\ \quad\quad\quad\ \ + NH_3 \\ CH_2—COOK \end{array}$$

$$\begin{array}{l} CH_2\,COOK \\ \quad\quad\quad\ \ + H_2SO_4 = \\ CH_2\,COOK \end{array} \begin{array}{l} CH_2\,COOH \\ \quad\quad\quad\ \ + K_2SO_4. \\ CH_2\,COOH \end{array}$$

Another portion of the pure crystals was tested for reduction

to pyrrol as follows: A small portion of the crystals was ground fine with zinc dust in an agate mortar, and the mixture then transferred to a very small distilling flask and heated over a Bunsen burner; the distillate was but a few drops, but the fumes turned a piece of pine moistened with hydrochloric acid bright red, showing unmistakably the presence of pyrrol.

Reaction is



Some of the crystals obtained from tubes 1, 2, and 3 are large and diamond-shaped when crystallized from ether and retain this characteristic diamond form even when recrystallized from methyl alcohol.

The lack of agreement in the melting points of succinimid and my crystals is explained by the length of the column of mercury outside the liquid in which the melting point was determined. The correction for this was found to be 1.8°, which would make my results agree with the accepted melting point of succinimid. To make sure that there was no mistake in this determination the melting point of some succinimid, made by the distillation of ammonium succinate, was found by my thermometer under the same conditions as obtained in the previous determination, to be 123° C.

Second Method. Acetonitril and Succinic Acid.—This method was tried to see whether the position of the COOH and CN groups had any effect on the reaction.

Tube No. 4. Succinic acid, 17.7 grams (one molecule), acetonitril, 12.3 grams (two molecules), and acetic anhydride four drops, were heating in a sealed tube for eight hours as described under tube No. 3. On cooling, this tube contained a black liquid but not as thick as the preceding. The contents were evaporated and extracted as before. Crystals were obtained which melted at 123° but were not entirely diamond-shaped. The yield in this case was nine grams but would probably have been larger had the tube been heated longer.

The pure crystals from this tube were treated with hot KOH and gave ammonia and succinic acid which was identified by its

melting point. They also gave pyrrol when distilled with zinc dust as in the previous case. Combustions for carbon, hydrogen and nitrogen were made with the following results:

Carbon and hydrogen: Weight substance, 0.2857 gram; weight CO_2, 0.5080; weight H_2O, 0.1382; equivalent to carbon, 48.49 per cent.; hydrogen, 5.37 per cent. Nitrogen: weight substance, 0.2787 gram; volume of nitrogen, 36.45 cc. at 27° C. and 766 mm.; pressure, equivalent to 14.54 per cent. nitrogen. (This figure is too high as NaOH was used to absorb the CO_2 because the KOH had given out.)

The crystals from this tube are undoubtedly identical with those obtained from Nos. 1, 2, and 3, and are formed according to the following reaction:

$$CH_3CN + (CH_2COOH)_2 = (CH_2)_2(CO)_2NH + CH_3COOH.$$

The second molecule of acetonitril plays no part in the reaction but was used to make the experiment as far as possible the reverse of No. 3.

I had hoped that these experiments might throw some light on the molecular arrangement of succinimid, but think they have not. Though the succinimid produced is undoubtedly identical with that formed by the distillation of ammonium succinate, and is probably symmetrical on account of its reduction to pyrrol, and is formed invariably to whichever radical the cyanogen group is attached, still I think, considering the analogy of phtalimid, that if an unsymmetrical succinimid were produced at first, that under the conditions of heat and pressure it would be converted into the more stable symmetrical compound.

Third Method. Ethylene Cyanide and Succinic Acid.—Tube No. 5 contained ethylene cyanide, eight grams, (one molecule); succinic acid, 11.8 grams, (one molecule); acetic anhydride, two drops. This tube was heated for six hours at a temperature of about 200° C. On opening, considerable pressure was observed and the contents were solid and semi-crystalline. The hard mass was extracted with ether as before; the crystals were partly diamond-shaped and partly rhombic octahedra; some had flat,diamond-shaped bases, and a pyramid on top, showing that the diamond-shaped crystals were but modifications of the rhombic octahedra, the ordinary crystalline form of succinimid.

According to the reaction

$$\begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} + \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} = 2 \begin{array}{l} CH_2C{=}O \\ | \quad \diagdown NH \\ CH_2C{=}O \end{array}$$ the

theoretical yield would be 19.8 grams. 16.2 grams, or 81.8 per cent. of the theoretical were obtained. The residue of carbon weighed 1.7 grams, which would be equivalent to 3.5 grams of succinimid, so that the loss due to manipulation was only 0.1 gram.

Two determinations of the melting point of the succinimid from this tube gave 122° C., or corrected, 123.8° C. The crystals also gave on distillation with zinc dust, pyrrol as before. Prof. Moses, of the School of Mines, very kindly measured the crystals obtained. The results were as follows:

$$a : b : c = 0.8044 : 1 : 1.471.$$

Some allowances must be made on account of the hollow faces of these crystals in comparing these figures with those of Bunge:[1]

$$a : b : c = 0.7888 : 1 : 1.3655.$$

Molecular Weight Determinations.—In order to determine that the molecular weight of succinimid was not a multiple of that ascribed to it (99), it was determined by Raoult's method, using water and glacial acetic acid as solvents. The method pursued was that given in Wiedermann and Ebert's Physikalisches Praktikum, Braunschweig, 1890.

First determination. In this experiment water was used as a solvent; the freezing mixture was snow and hydrochloric acid; the substance used was made by the action of acetonitril on succinic acid (tube No. 4).

The thermometer was set for water by changing the amount of mercury in the column, and then the freezing point of distilled water was determined twice. Both determinations gave 2.40 on the Beckman thermometer. 8.0449 grams of water were used which filled the portion of the tube in the freezing mixture; after the second determination the ice was allowed to melt and 0.1146 grams of the substance introduced through the side tube; when this had dissolved completely, which required an hour and a half, the mixture was again chilled; the mercury went down gradually to 0.8° and then rose rapidly to 2.12° where it remained

[1] *Ann. Chem.*, (Leibig), Suppl., 7, 118, *1870*.

stationary for some time; after making sure that this was the correct reading, the mixture was allowed to melt and a second addition of 0.1153 gram of substance introduced as before. The process was repeated and the freezing point found to be 1.84°; using for water the value 18.5, the calculation is as follows:

$M = \frac{\Gamma}{e}$ or M, the molecular weight, is equal to the constant determined for water by use of known substances divided by e the depression in degrees centigrade produced by one gram of the substance dissolved in 100 grams of water. To obtain e we have the following proportions for the first addition:

$$0.1146 : 8.0449 :: X : 100.$$

X, number of grams per hundred grams of solvent in the solution used, 1.424.

$$1.4245 : 1 :: 0.28 : e \qquad e = 0.1965°$$

Substituting in formula $M = \frac{\Gamma}{e} = \frac{18.5}{0.1965}$ or $M = 94.1$. For the second addition:

$$0.2299 : 8.0449 :: X : 100 \qquad X = 2.8577$$
$$2.8577 : 1 :: 0.56 : e \qquad e = 0.1959° \qquad M = 94.4$$

Though the results were sufficiently accurate to show that the formula of succinimid was not a multiple of ninety-nine, further experiments were made to confirm them and to obtain results with some other solvent as a check.

Benzene was tried but though a much smaller amount of substance was used, it was not sufficiently soluble to give any satisfactory results. On chilling the mixture, the succinimid gradually separated out and the thermometer did not go down regularly below the freezing point and then rise to and remain at a definite place, but went down continually by jerks. In determining the freezing point of benzene, snow and a little salt was used and it was found inadvisable to have the freezing mixture more than 10° below the freezing point of the solvent.

Ethylene bromide was next tried but exactly the same difficulty was encountered as with benzene. Water was again used as a solvent and the following figures were obtained with crystals from tube No. 3.

Weight of solvent, 9.6352; freezing point, 4.72°.

First addition: Weight substance, 0.0536; freezing point, 4.626°; e = 0.1689; M = 109.4.

Second addition: Weight substance, 0.0536 + 0.0568 = 0,1104; freezing point, 4.55°; e = 0.1485; M = 124.6.

Third addition: Weight substance, 0.0536 + 0.0568 + 0.0586 = 0.1690; freezing point, 4.395°; e = 0.1853; M = 99.8.

Fourth addition: Weight substance, 0.2224; freezing point, 4.22°; e = 0.2168; M = 85.3

Determinations Using Acetic Acid.—99.5 per cent. acetic acid was used in this work and the figure 38.6 (taken from Ostwald on Solution, page 229) was employed. A new difficulty was encountered in these determinations, which was that the acetic acid froze at a lower temperature each time; successive determinations gave the following figures: 2.17°, 2.13°, 2.105°, 2.08°. The explanation of this is that the acetic acid is constantly becoming weaker and the greater proportion of water gives a lower freezing point. In making the determination it was therefore necessary to estimate the probable depression due to evaporation and subtract it from that observed.

The determination was made substantially as before except that cold water was used instead of the freezing mixture. As the lowering of the freezing point of the acetic acid seemed to grow slightly less on successive freezings, the probable freezing points for the next three determinations were estimated at 2.055°, 2.035°, and 2.015°, respectively. Weight of acetic acid, 12.1795 grams; weight of substance (succinimid from tube No. 3), 0.0700.

Second determination on first addition: Freezing point 1.81°; e = 0.3893; M = 99.1. Second addition: Weight solvent, 12.1795 grams; weight of substance, 0.0700 + 0.0965 = 0.1665; freezing point, 1.50°; depression, 0.515; e = 0.3840; M = 100.5.

The average of two determinations on substance from tube No. 4 is 94.25, using water as the solvent.

The average of four determinations on substance from tube No. 3 is 104.8 (solvent water).

The average of two determinations on same, using acetic acid as the solvent, is 99.8.

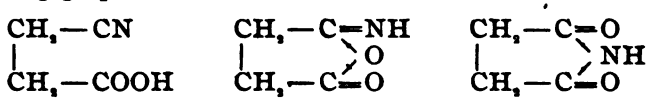
General average, 99.61.

Conclusions.—Succinimid has been made as follows:

1. By the action of ammonia on succinic anhydride. (D'Arcet.)
2. By passing ammonia over melted succinic acid. (Fehling.)
3. By the distillation of ammonium succinate. (Fehling.)
4. By the distillation of acid ammonium succinate. (Fehling.)
5. By the distillation of succinic acid and acetamide. (Menshutkin.)
6. By heating ethylene cyanide and acetic acid in a sealed tube.
7. By heating in the same way acetonitril and succinic acid.
8. By heating, as above, ethylene cyanide and succinic acid.
9. Methyl succinimid has been made by the action of sulphuric acid on isonitrosovalerianic acid.

There seems to be no doubt that the succinimid produced by all these methods is identical. Its molecular weight and percentage composition show that the formula must be $C_4H_5NO_2$.

For its molecular arrangement, we have to choose between the following graphic formulae:



The first is inadmissible as it is shown by Landsberg that the ethyl ether on decomposition gives ethylamine, while the ethyl ether of β cyanpropionic acid would give ethyl alcohol; it also seems to me that β cyanpropionic acid would turn methyl-orange pink as cyanacetic acid does, but as succinimid does not.

Between the last two, the facts that succinimid on reduction with zinc dust gives pyrrol and with alcohol and sodium pyrrolidin and that succinimid is formed invariably to whichever radicle the CN and COOH groups are attached, are the most important evidences in favor of the symmetrical arrangement. We would also expect that the symmetrical would be the more stable compound. This is borne out by the well-known stability of succinimid, which can be distilled without decomposition.

I believe that succinimid is symmetrical as all the facts observed point to that conclusion; but I think it cannot be proved absolutely until its specific refractive power is determined, which will show in connection with the specific refractive powers of the other elements and with that of nitrogen when

joined in different ways, whether, in the case of succinimid, it is attached to one or two carbon atoms.

If β cyanpropionic acid could be isolated, it might on heating be converted into the isomeric unsymmetrical succinimid, and it was with a view to this that the attempts to make this acid, described in part third, were undertaken.

PART III.

ATTEMPTS TO MAKE AND ISOLATE β CYANPROPIONIC ACID BY THE ACTION OF POTASSIUM CYANIDE ON β IODOPROPIONIC ACID.

No. 1. Seventy-five grams of β iodopropionic acid were dissolved in ninety cc. of hot water and neutralized with thirty-four grams of potassium carbonate, then thirty-five grams of finely pulverized potassium cyanide were added and the solution stirred till it dissolved. It was next evaporated and stirred continuously with a thermometer till the temperature reached 132° C. During this time some hydrocyanic acid was given off; the mass was dissolved in a little hot water and neutralized with hydrochloric acid, then evaporated on a water-bath to a syrupy mass and shaken with ether. The ether extract on evaporation yielded nothing.

Before the experiment could be repeated, it was necessary for a new supply of β iodopropionic acid to be made from glyceric acid, and as no phosphorous di-iodide was to be obtained, that had to be prepared also.

After having secured a supply of the iodo acid, the attempts to convert it into the cyan acid were resumed.

No. 2. Fifty grams of β iodopropionic acid were dissolved in a little hot water and 22.8 grams of finely pulverized potassium carbonate added and the carbonic acid boiled out; 21.66 grams of potassium cyanide were dissolved in as little hot water as possible and added to the solution now containing the potassium salt of β iodopropionic acid. The solution was allowed to stand over night and then boiled with a return condenser for five

hours, in an endeavor to ensure the formation of KI and cyanpropionic acid. The liquid was then put in an evaporating dish and neutralized with a calculated quantity of normal sulphuric acid and shaken with ether many times, the ether being recovered and used repeatedly, the residues from which the ether was distilled, were dissolved in water and shaken with lead carbonate separately. This gave an effervescence showing the formation of the lead salt of an acid and also of some lead sulphate. These several mixtures were each filtered and then saturated with hydrogen sulphide to precipitate the lead and set free the cyan acid. The lead sulphide was filtered out and the solution evaporated as far as possible on a water-bath. It was then put in a desiccator under diminished pressure over sulphuric acid and left for twenty-four hours. At the end of that time needle-like crystals appeared; they were left there for several days longer and the crystals were subsequently removed and dried between filter paper.

The crystals were white and small and not over 0.100 gram in weight. This method seemed an improvement over the use of hydrochloric acid but the yield was so extremely small as to be rather discouraging.

No. 3. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate added until the solution was alkaline. It was then warmed on a water-bath till the effervescence ceased when nine grams of freshly pulverized potassium cyanide were added and the mixture heated till it was dissolved. In this way the amount of water present was reduced to a minimum. It was evaporated to a syrup on a water-bath and heated over a flame until the temperature reached 125° C. It was next transferred to a beaker and made acid by the addition of three cc. of concentrated sulphuric acid previously diluted with water. Carbon dioxide was given off as before. It was then shaken with large quantities of ether to extract the free acid and let stand for four weeks before the ether was distilled off. The residue was similar to that obtained by No. 2, but the quantity was very small.

No. 4. Twenty-five grams of β iodopropionic acid were dissolved in hot water and potassium carbonate was added until the

reaction was alkaline, which required 19.75 grams owing to the poor quality of the iodo acid used. 11.4 grams of finely ground potassium cyanide were added and the solution warmed till it dissolved. The solution was at this time straw colored and was heated to boiling and boiled for about a minute, when it became dark reddish brown and smelled of hydrocyanic acid. The heating was stopped here, as the destruction of the compound by overheating was feared.

8.12 cc. of concentrated sulphuric acid diluted with thirty cc. of water were added which gave a lively effervescence of hydrocyanic acid. It was evaporated carefully over a flame and the sticky mass put in a continuous extractor and extracted for several hours. The ether was finally evaporated and the yellowish crystalline residue was dissolved in methyl alcohol which was put aside to crystallize. From this lot were obtained 0.200 gram of good crystals.

No. 5. The same method was tried again but the mass was heated to 135° instead of 125° and the acid was not added until after the evaporation. Twenty-five grams of β iodopropionic acid of good quality were dissolved in twenty-five cc. of hot water and neutralized with 10.15 grams of finely pulverized potassium carbonate; after it was warmed to drive out carbon dioxide, 11.35 grams of ground potassium cyanide were added. The mixture was placed on the water-bath to react for three hours. It was then heated over a flame until the temperature reached 135° after which it was allowed to cool and 4.17 cc. of concentrated sulphuric acid diluted with fifteen cc. of water were added. There was some smell of hydrocyanic acid but not so much as in No. 4. This was next evaporated rapidly over a flame till the mass was only slightly sticky, transferred to an extractor and extracted with ether for four hours. The residue was tested and found to be potassium cyanide and iodide. The ether solution was distilled and the residue recrystallized from methyl alcohol as before. The yield was small as usual.

No. 6. The effect of pressure as well as heat was tried in this and the following experiment:

Two lots of ten grams each of β iodopropionic acid were weighed out and mixed with 3.46 grams of fine potassium car-

bonate. To this, water was added and the whole warmed until it dissolved. Then 3.28 grams of potassium cyanide were dissolved in water and added to each, and the resulting solutions put in tubes. On standing, the solutions became dark colored; they were sealed and heated for three hours at 112° C., then allowed to cool. A black film appeared on the inside of the tubes similar to that deposited on the flask when boiled with a return condenser. They were heated three hours longer at the same temperature and examined; the contents seemed to be turning solid. The tubes were heated again for seven hours and when opened there was no perceptible pressure.

The contents of the two tubes were combined and evaporated on a water-bath to a syrup and enough sulphuric acid added to neutralize all the potassium carbonate. There was no effervescence whatever which was encouraging as it indicated that the potassium cyanide had been converted into iodide. It was replaced on the water-bath to evaporate, and when dry, extracted in a continuous extractor for six hours. The ether was then distilled and the residue of nearly white needle-shaped crystals dissolved in methyl alcohol and set aside to crystallize. After four days the crystals were dried and their melting point was found to be 165° The yield was 0.658 gram; theory, 5.1.

No. 7. This experiment differs from the preceding in that two molecules of potassium cyanide were used instead of potassium carbonate; one to form the potassium salt of the acid and the other to furnish the CN group.

Two portions of five grams each of β iodopropionic acid were weighed out, and to them were added 3.28 grams of potassium cyanide, dissolved in eight cc. of water. This produced an effervescence of hydrocyanic acid. It was transferred to tubes and allowed to stand for several hours, during which time the solution became dark reddish brown in color. These tubes were heated the same as No. 6 and appeared about the same. They were combined and evaporated as before, and enough of sulphuric acid added to satisfy one-half the potassium cyanide. The contents of the two tubes were extraced with ether as previously described, the crystals looked about the same as those obtained by No. 6 and melted at 162° C. The yield was 0.175 gram; theory, 2.9 grams.

ATTEMPTS TO MAKE β CYANPROPIONIC ACID FROM ETHYL ETHER OF β IODOPROPIONIC ACID.

No. 8. As the ethyl ether of chloracetic acid on treatment with potassium cyanide gives cyanacetic acid, it seemed probable that the ethyl ether of β iodopropionic acid would give β cyanpropionic acid. It was with this hope that the following experiments were undertaken.

The iodo acid had first to be converted into the ether which was done as follows: 200 grams of β iodopropionic acid, 100 grams of ethyl alcohol, and twenty grams of sulphuric acid were mixed in a round-bottomed flask and heated on a water-bath with a return condenser for five and a half hours. The liquid had then separated into two layers. It was transferred to a separator and washed, first with sodium carbonate solution and then with water. The ether, a dark, heavy liquid, was then separated and dried. The yield was 125 grams.

To convert the ether into the cyan acid I used an excess of potassium cyanide over the two molecules required by the reaction.

$$CH_2ICH_2COOC_2H_5 + 2KCN = CH_2CNCH_2COOK + KI + C_2H_5CN.$$

To 145 grams of the ether were added ninety-three grams of potassium cyanide dissolved in 372 grams of water. This mixture was made in a round-bottomed flask in which it was left to stand for twenty hours, the ether forming a separate layer. It was then heated with a return condenser for ten hours; at the end of five hours the layers had mixed and the whole solution was a dark brown in color. On removing from the flask, a dark oil was seen floating on the liquid and to obtain this it was shaken with ether twice, the ether extracts separated, and the ether distilled off; the residue was a brown oil which was tested for nitrogen by the prussian blue reaction but none was found. It, however, gave a decisive test for iodine, and was the unaltered ether of β iodopropionic acid.

The solution from which the unaltered ether had been removed was made almost neutral with sulphuric acid and evaporated on a water-bath to dryness. It was then made acid with dilute (normal) sulphuric acid and shaken twice with liberal quantities of ether. The residue, a brown liquid, was made strongly acid

with sulphuric acid and shaken with ether three times. The residue from this treatment was evaporated to dryness on a water-bath and extracted with ether three times more.

The three different ether solutions, supposed to contain the cyan acid, were distilled separately and the residues kept to convert into the lead salt of cyanpropionic acid as a means of purifying the product. To do this they were shaken with lead carbonate in excess and then the lead sulphate and carbonate filtered out. The formation of the lead salt gave a lively effervescence with the first two lots but failed to give any with the third, so I considered that none of the cyan acid was removed by the last extractions.

The filtrates described above were saturated separately with hydrogen sulphide, which gave a copious precipitate of lead sulphide. The solutions were filtered and the filtrates combined and evaporated on a water-bath to dryness. It was then found that the lead had not been entirely removed, so the mass was redissolved in hot water, and hydrogen sulphide passed in again. It was filtered and washed as before and evaporated on a water-bath. On cooling, the substance turned solid.

The solubility of this substance is as follows:

	Cold.	Warm.
Ether	insoluble	almost insoluble
Ethyl alcohol	slowly soluble	soluble
Chloroform	insoluble	insoluble
Carbon disulphide	insoluble	insoluble
Methyl alcohol	insoluble	soluble
Acetone	insoluble	insoluble
Benzene	insoluble	insoluble

Some of this product was recrystallized from both ethyl and methyl alcohol and the melting points determined. The results were as follows:

Ethyl alcohol	110°–111°
Methyl alcohol	109°–110°
Crude	154°

A small sample was recrystallized from methyl alcohol several times and its melting point determined. It began to melt at 117° but part remained solid until 144° was reached, when all melted, indicating in spite of repeated recrystallizations that the sample was a mixture.

No. 9. This method is a slight modification of the preceding. Ninety grams of potassium cyanide were dissolved in 300 cc. of water and added to 142 grams of the ethyl ether of β iodopropionic acid in a round-bottomed flask as before. This was heated on a water-bath with a return condenser for twelve hours to try to ensure the entire conversion of the ether; it was then shaken with ether in a separator to recover the unaltered ether, and in spite of the increased time during which the mixture was heated thirty-five grams of the ether were obtained.

The under layer from the separator was neutralized with sulphuric acid and evaporated on a water-bath to a syrup. It was made acid with dilute sulphuric acid (one to one) and shaken with ether in a separator three times, using liberal amounts of ether each time.

(The object of first neutralizing and afterwards making acid was to avoid as far as possible, heating with acid which might form succinic acid.) The ether solutions were of a dark reddish color, much darker than those obtained in No. 8. The ether was distilled off, the residue diluted with water, shaken with lead carbonate, filtered, washed, the filtrate saturated with hydrogen sulphide as before, the lead sulphide filtered out and the solution evaporated on the water-bath.

The residue from the ether extraction was evaporated on a water-bath until on cooling it turned solid, and was then transferred to a separator and made much more strongly acid with dilute sulphuric acid, and was well mixed and shaken three times with ether. The ether solution was treated as before, and after removing the lead, was added to the first portion and evaporated to dryness with it. The solid mass was then crystallized twice from methyl alcohol.

To the residue from the second ether extraction in the separator, water was added and the solution filtered, the residue was rejected, and to the filtrate, litharge and lead carbonate added until all the acid present which was mostly sulphuric was neutralized. It was next filtered and hydrogen sulphide passed in. A precipitate of a dark red brown color was obtained instead of the black lead sulphide. This precipitate was filtered out and was found to contain lead and sulphur, was soluble in hot

dilute nitric acid and in concentrated hydrochloric acid, but insoluble in dilute sulphuric. This red precipitate sometimes forms at other times when the solution supposed to contain the lead salt of β cyanpropionic acid is saturated with hydrogen sulphide, but it was always either subsequently decomposed or obscured by the quantities of black sulphide which formed later.

This compound is apparently similar to the lead chlorosulphide described by Fresenius (page 173 Qual. Anal.), but in which some organic acid replaces the hydrochloric acid.

The filtrate from this precipitate was evaporated to dryness on the water-bath and extracted with ether four times. The ether was distilled off and the resulting crystals recrystallized from methyl alcohol.

Total yield, 2.6 grams, having a melting point of 124° C.

INVESTIGATION OF CRYSTALS MADE BY THE PRECEDING METHODS.

Combustions were made on the crystals obtained by methods 8 and 9. The amount of moisture was also determined by drying so as to calculate the percentage to the dry if possible. The results were as follows:

No. 8 gave—

Carbon	38.95 per cent.
Hydrogen	6.39 " "
Nitrogen	11.62 " "
Loss on drying for five hours at from 90° to 107°	12.31 " "
Nitrogen, on dried sample	8.07 " "

These results calculated to the dry measure gave—

Carbon	44.42 per cent.
Hydrogen	5.72 " "
Nitrogen	13.25 " "

These combustions were made very carefully and I believe them to be correct. The figures agree quite closely with the percentage composition of $C_6H_{12}N_2O_4$, which is

Carbon	44.44 per cent.
Hydrogen	5.55 " "
Nitrogen	12.97 " "

This might be formed by two molecules of β cyanpropionic acid taking up one molecule of water and combining, $2C_4H_5NO_2 +$

$H_2O = C_8H_{12}N_2O_5$, or it may be written $C_4H_5NO_2 + \frac{1}{2}H_2O$. The melting point of crystals from No. 8, on which these combustions were made, was 110° C.

No. 9 gave—

Carbon	37.15	per cent.
"	37.27	" "
Nitrogen	6.34	" "
"	6.19	" "
Hydrogen	5.77	" "
"	5.79	" "

Loss on drying to constant weight for eighteen hours at 100°–110°, 13.22 per cent.

These determinations of the carbon, hydrogen, and nitrogen, calculated to the dry gave—

Carbon	42.88	per cent.
Hydrogen	4.96	" "
Nitrogen	7.22	" "

A nitrogen combustion was made on the crystals from Nos. 6 and 7, which gave further evidence of the loss of nitrogen by heating as the crystals obtained by these methods contained but 3.02 per cent. nitrogen.

The crystals from methods 8 and 9 were dissolved in water and tested with methyl orange to see whether they would give an acid reaction, but they did not. They only gave the color of a neutral solution. Succinimid (M. P. 124) was tried which gave the same color. Cyanacetic acid was also tried but this gave a bright pink. From this it was evident that the crystals could not be β cyanpropionic acid or they would turn the indicator like cyan acid.

The mother liquor from method No. 5, in which the crystals were slowly forming, was tested in the same way and it gave a decided pink color. To make sure this was not due to any mineral acid, I tested for sulphuric acid with barium nitrate but found none. (Sulphuric was the only acid used in the method.)

I now believe that β cyanpropionic acid is a liquid and is formed in many of the preceding methods, but that it decomposes very readily by heat or pressure, forming various complicated organic compounds, which are the crystals obtained. Another reason for my thinking so is that methods 6 and 7 which

are heated in sealed tubes, on evaporating gave crystals direct, while in the methods which were not heated so much a syrupy liquid was left, which only deposited crystals after standing in some cases for weeks over sulphuric acid, showing the complete decomposition of the acid in the first case and but the partial in the second as it was there the acid reaction was obtained. The irregularity of the combustion is explained by the fact that the samples must have been in most cases, mixtures. The only combustions which agree very well are those made on the same day on a sample of No. 9 which had been recrystallized four times.

The diminished percentage of nitrogen in the methods where longer or higher heat was used, and also where the sample was afterwards dried, seems to be invariable and points to a decomposition in which nitrogen is lost.

The nearest approach to β cyanpropionic acid so far produced is its ethyl ether which has been made by L. Henry,[1] as follows:

Heat $CH_2ICH_2COOC_2H_5$ with potassium cyanide dissolved in alcohol in slight excess on a water-bath with a return condenser. The reaction takes place easily and potassium iodide is deposited abundantly; at the end the liquid turns brown. Drive out as much of the alcohol as possible by distilling on the water-bath and extract the cyan ether with ordinary ether. The distillation of the ether solution gives the pure cyanpropionic ether. The yield is almost theoretical.

The cyanpropionic ether is a colorless liquid, without odor, insoluble in and more dense than water, and boils at 228°. Caustic potash in aqueous alcohol transforms it easily into normal potassium succinate. With aqueous ammonia it gives cyanpropionic amide $CN(CH_2)_2CONH_2$.

The preceding facts were not known to me at the time I made my experiments on iodopropionic ethyl ether or I should have tried alcoholic cyanide, and so by the elimination of water, would have probably succeeded in obtaining the ethyl ether and amide of β cyanpropionic acid, if not the acid.

My experiments show that the β iodopropionic ethyl ether does not act with potassium cyanide like the ethyl ether of chloracetic, as by treating the latter with potassium cyanide as

[1] L. Henry, *Bull d. l'acad. royal de Belgique*, [3] 18, 168, *1889*.

described under the first method in which the ether was used, I obtained a good yield of cyanacetic acid without difficulty.

The reactions between nitriles and both fatty and aromatic acids will be more fully developed in this laboratory.

ORGANIC LABORATORY, SCHOOL OF MINES,
COLUMBIA COLLEGE, MARCH, 1894.

THE DETERMINATION OF PHOSPHORIC ACID.

BY S. W JOHNSON.

Received April 25, 1894.

THE papers on determination of phosphorus in steel by Messrs. Dudley and Pease, by Mr. Handy, and by Messrs. Doolittle and Eavenson, remind me of some work done at my instigation in the years 1880, 1889, and 1890, and published in the Annual Reports of the Connecticut Agricultural Experiment Station for those years.

In 1880, Mr. (now Professor) H. L. Wells, demonstrated that the citrate method for determining phosphoric acid may give good results under certain conditions, but that the results are correct because of a compensation of errors, the ammonium magnesium phosphate not carrying down quite all the phosphorus but containing enough impurities to counterbalance that loss. Over ninety determinations were made, many of them in duplicate, on forty different substances (fertilizers), after a large number of preliminary trials had indicated the effect of varying the several conditions which might influence the results. In most cases the percentages of phosphoric acid found in duplicate agreed well together and also agreed fairly with those given by the molybdate method. In a few cases, however, considerable discrepancies appeared and it was evident that further study was needful before the citrate method could be fully trusted for fertilizer work.

In 1889, in conjunction with Dr. T. B. Osborne, investigation of the citrate method was resumed. The German agricultural chemists were beginning to use it and J. H. Vogel had published details of procedure. We found that Vogel's process gave results too low and not closely agreeing with the molybdate method. By using more and stronger magnesium mixture and a larger quantity of concentrated ammonia, we overcame this discrepancy, and in sixty-seven determinations on bone-dust superphosphates, cotton-hull ashes, cotton-seed meal, tankage,

bone char, phosphatic guano, and phosphate rock, we found that but three citrate determinations differed from those by molybdate, by more than 0.3 per cent., and but four others by more than 0.2 per cent. The greatest discrepancy between the two methods was 0.41 per cent., while the average difference was 0.09 per cent. In thirty cases the citrate method averaged 0.117 per cent. more, in thirty-three cases 0.079 per cent. less, than the molybdate method. These percentages were reckoned on 0.4 gram of substance containing from 0.5 to 31.5 per cent. of P_2O_5. The determinations were not made with unusual care, but were turned off rapidly as a part of the routine work of the station.

The citrate method was found to give unsatisfactory results where iron and alumina were present in considerable quantity, as in case of "Grand Cayman's Rock," "Thomas Gilchrist Slag," and "Keystone Phosphate." A series of trials under varied conditions was made in 1889 with the hope to ascertain the cause of the discrepancies but without success.

Some analyses of the ignited precipitate obtained by the citrate method may be quoted here:

COMPOSITION OF IGNITED "CITRATE PRECIPITATES."

	Bone.	Super-phosphate.	Grand Cayman's phosphate.	South Carolina rock.	Bolivian guano.	Dissolved bone black.
Carbon	0.41	0.19	0.44	0.15	0.48	0.27
Silica		0.12	0.40	0.10	0.24	0.19
Calcium oxide	2.59	2.13	2.05	3.21	3.95	2.05
Magnesium pyrophosphate	95.49	96.07	95.66	95.77	94.98	97.83
Ferric and aluminum phosphate			0.71	0.35		0.31
Loss	1.51	1.49	0.74	0.42	0.35	
	100.00	100.00	100.00	100.00	100.00	100.65

The loss probably consisted in part, of magnesia and in part also of pyrophosphoric acid. It is seen that the ignited precipitates contained from two to four per cent. of lime, that iron and alumina entered into the precipitate in small quantity when these elements were abundant in the original substance, and that where there was little or no loss, the recovered phosphoric acid amounted to from 95 to 97.8 per cent. of the precipitate.

In case of Grand Cayman's phosphate rock, duplicate determinations differed as much as 0.3 per cent., and the variations of duplicates of Thomas Slag and Keystone phosphate were even greater. It was also found that by changing the proportions of the reagents and by using on the one hand moderate and on the other vigorous and prolonged agitation, the quantity of phosphoric acid, reckoned from the ignited precipitate, fluctuated, in case of Thomas slag and Keystone phosphate, $2\frac{1}{2}$ and $3\frac{1}{2}$ per cent., respectively, although by using large quantities of magnesia mixture and of strong ammonia, accordant and high results were realized.

Thus far we employed the modified rapid molybdate method, precipitating from hot solutions and digesting for one hour at 65° C. Finally in 1890 we found that under this procedure, the molybdate method, though satisfactory in absence of ferric, aluminum, and manganese salts, is, in their presence, little better than the citrate method. In case of Keystone phosphate three determinations by Osborne, using the U. S. "official" method gave figures ranging from 45.25 to 46.68 per cent.!

It was therefore necessary to return to the original Sonnenschein method and make the precipitations at 40° to 50° C., during six hours. Six determinations thus carried out by Osborne, gave results from 44.67 to 44.86, the average being 44.82 per cent.

Comparative duplicate trials on a carefully made up solution of known composition with $P_2O_5 = 18.93$ per cent.[1] (from crystallized sodium phosphate) $Fe_2O_3 = 20$ per cent., $Al_2O_3 = 4.72$ per cent., and $MnO = 5.09$ per cent. (from sulphates), yielded Osborne, by the original Sonnenschein method, 18.92 and 18.94 per cent., and by the "official" method 19.26 and 19.26 per cent.!

We proved that with relative excess of nitric acid or relative deficiency of molybdic acid, a portion of phosphoric acid may easily fail to be thrown down. We also found that when precipitation is made hot and digestion is conducted at 65° C., ferric iron, and aluminum, if present, are to some extent included in the yellow precipitate and when this is dissolved in the subsequent treatment with ammonia, they pass into the alkaline

[1] Determined in the usual manner as magnesium pyrophosphate.

solution and thence into the ammonium-magnesium phosphate.

To sum up, the citrate method only gives good results by compensation of its errors and under exactly defined conditions which must be empirically determined. A procedure good for calcium phosphates is quite inapplicable to ferric and aluminum phosphates.

Again, the molybdic method, when carried out rapidly at temperatures higher than 50°, or as high as 65° C. in presence of trivalent iron, aluminum, or manganese, gives results too high, and in presence of great excess of nitric acid may give results too low, unless the filtrates from the yellow precipitate are mixed with additional molybdic solution and further digested until no more precipitate can be thrown down.

DOUBLE BROMIDES OF PALLADIUM.

By Edgar F. Smith and Daniel L. Wallace.

Received May 5, 1894.

BONSDORFF (*Poggendorff's Annalen der Physik*, [1], N. F., **19**, 347) was one of the first chemists to attempt the preparation of double halides of palladium with other metals. Beyond mere mention of the fact that he obtained palladium bromide by the action of a mixture of nitric and hydrobromic acids upon the metal, that the resulting compound apparently combined "mit den Bromiden elektro-positiver Metalle," and that he made double salts of it with the chlorides of potassium, barium, manganese, and zinc, we have not discovered any additional literature relating to the above subject. It does not appear that Bonsdorff analyzed any of the double halides obtained by him.

Desirous of finding a salt or salts of palladium suitable for, but as yet not used in atomic mass determinations of palladium, we took occasion to prepare several double bromides of that metal, hoping to find among them one or more which might be available for the purpose.

Very pure metallic palladium was dissolved in nitro-hydrobromic acid. The residue was moistened with hydrobromic acid and repeatedly evaporated to dryness upon a water-bath. The palladium bromide, reddish-brown in color, was only soluble in water containing hydrobromic acid. Weighed quantities of this

dry bromide, with equivalent amounts of the metallic bromides, were dissolved in water containing hydrobromic acid. Upon evaporation, crystalline residues were obtained. These were always dissolved in water and again allowed to separate.

POTASSIUM PALLADIUM BROMIDE.

K_2PdBr_4.

This salt separated from its aqueous solution in shining reddish-brown needles. It is anhydrous. It is very stable and suffers no change on exposure to the air. In analyzing it we determined the palladium by the method suggested by Frenkel, *Ztschr. anorg. Chem.*, **1**, 229. By following this recommendation the bromine can be precipitated by silver nitrate without contamination with palladium.

Analysis.—0.4930 gram dried material gave 0.1045 gram metallic palladium, equal to 21.19 per cent. Pd, and 0.7428 gram silver bromide, equal to 63.79 per cent. Br, while the theoretical requirements of K_2PdBr_4 are 21.12 per cent. Pd and 63.50 per cent. Br. A second portion of substance, weighing 0.2613 gram, was gently heated in a current of hydrogen and, after cooling, the residue was extracted with hot water. Upon evaporating this aqueous solution to dryness, 0.1251 gram of potassium bromide was obtained. This is equal in percentage to 15.58 per cent., while the theoretical potassium bromide in this double salt is 15.45 per cent.

Hoping that by adding bromine to the aqueous solution of the above salt, and digesting the same with this reagent, at a temperature not exceeding 70°, we might possibly get a salt of the formula K_2PdBr_6, we carried out several such experiments. The result was not what was anticipated; the product being really a salt of the simpler type, K_2PdBr_4, with two molecules of water of crystallization, $K_2PdBr_4 + 2H_2O$. It separated in long, dark-brown and shining needles, which on exposure rapidly lose their luster, become dull, and acquire a reddish-brown color. Owing to the rapid loss of water by the crystals, the analytical results do not approach the theoretical requirements as closelv as might be expected.

Analysis.—0.3235 gram substance gave 0.0660 gram, or 20.37 per cent. of metallic palladium; 0.4565 gram of silver bromide,

equal to 60.00 per cent. of bromine and 0.0201 gram of water, equivalent to 6.21 per cent. The formula $K_2PdBr_4 + 2H_2O$ requires 19.71 per cent. Pd, 59.2 per cent. Br, and 6.65 per cent. H_2O.

AMMONIUM PALLADIUM BROMIDE.

$(NH_4)_2PdBr_4$

This salt crystallizes in beautiful and quite large olive-brown colored forms which apparently possess an orthorhombic habitus. They are anhydrous and are perfectly stable in ordinary air. They possess about the same solubility as the corresponding potassium salt.

Analysis.—0.2528 gram dry material gave 0.0585 gram metallic palladium, equal to 23.14 per cent., and 0.4090 gram silver bromide, equivalent to 68.82 per cent. of bromine, while the theoretical percentages are Pd = 22.91, and Br = 69.17.

As this salt and the corresponding potassium salt are anhydrous and can be obtained pure without great difficulty, it is our intention to use them in a redetermination of the atomic mass of palladium.

SODIUM PALLADIUM BROMIDE.

We experienced much trouble in getting this salt, and it was only after the solution, containing equivalent amounts of sodium and palladium bromides, was allowed to remain in a vacuum desiccator over concentrated sulphuric acid for some time that it separated out in large deep red colored plates which proved to be very deliquescent. It was therefore necessary to conduct the analysis with imperfectly dried material. Through an accident we are not able to give a result upon the bromine content, and are limited to a presentation of the palladium and water percentages. These are, 19.68 per cent. Pd, and 14.67 per cent. H_2O. A salt of the composition $Na_2PdBr_4 + 4\frac{1}{2}H_2O$ would require 19.25 per cent. Pd, and 14.63 per cent. H_2O.

This salt is very deliquescent and even to a much greater degree than the corresponding double chloride of sodium and palladium.

STRONTIUM PALLADIUM BROMIDE.

The solution of this salt also stood for many days before crystals made their appearance. It consists of short, black prisms, which are stable on exposure to the air.

Analysis.—0.2256 gram air-dried substance gave 0.0366 gram Pd, or 16.22 per cent.; 0.2643 gram silver bromide, or 49.82 per cent. Br, and 0.0679 gram strontium sulphate, equal to 14.09 per cent. strontium.

A second analysis gave 0.0518 gram Pd, or 16.79 per cent.; 0.3595 gram silver bromide, or 49.57 per cent. Br; 0.0861 gram strontium sulphate, equal to 13.29 per cent. Sr, and 0.0544 gram water, corresponding to 17.63 per cent.

A salt of the composition $SrBr_2.PdBr_2 + 6H_2O$ would require

17.11 per cent. Pd
13.99 " " Sr
51.47 " " Br
17.37 " " H_2O

Our deficiency in bromine, we believe, is due to a slight loss of that constituent occurring during the drying process.

MANGANESE PALLADIUM BROMIDE.

This salt is very soluble in water. Like the two preceding salts it only separated from its aqueous solution after long standing. Its crystalline form is apparently like that of the ammonium salt. The crystals are dull-black in color.

Analysis.—0.1829 gram air-dried substance was carefully heated to constant weight in an air-bath. The loss, representing water, equaled 20.39 per cent. The anhydrous residue was then exposed at a moderate temperature to the action of hydrogen gas. On cooling, the mass was extracted with dilute hydrochloric acid. The spongy palladium weighed 0.0331 gram, equal to 18.09 per cent. Pd. The filtrate from the palladium gave 9.29 per cent. of manganese.

These results indicate a salt with the formula $MnPdBr_4 + 7H_2O$, which would require

17.52 per cent. Pd
9.05 " " Mn
20.73 " " H_2O

An effort was made to prepare the double halides of zinc and of cadmium with palladium, but the products crystallized so poorly that the analysis of the same was abandoned.

UNIVERSITY OF PENNSYLVANIA,
April 25, 1894.

AN EXAMINATION OF THE CHLORIDES OF ZIRCONIUM.

By F. P. Venable.

Received April 16, 1894.

A ZIRCONIUM chloride of definite composition would prove a valuable compound for determining the atomic weight of the element. There are several difficulties in the way of securing such a compound.

1. The tendency to form basic chlorides.

2. The ease with which hydrochloric acid is lost through the action of heat and of dehydrating agents.

3. The presence of free hydrochloric acid.

4. The deliquescent nature of the chlorides.

It is particularly desirable that the conditions under which a definite chloride can be formed should be discovered, as zirconium seems to yield no very satisfactory compounds for the determination of the atomic weight. There have been many efforts at finding out these exact conditions.

Most text-books state that anhydrous, pure zirconium tetrachloride can be prepared by passing dry chlorine over a mixture of charcoal and zirconia heated to a high temperature. Hermann used this sublimed zirconium chloride for the determination of the atomic weight. As Clarke says, however, little confidence can be placed in his results. Bailey[1] has recorded that even with great care to avoid the presence of moisture he was unable to prevent the formation of oxychlorides. He also says that in no case was it found possible to prepare the chloride free from iron and silica. The necessity for the presence of these in the materials used or in the resulting compounds is not very apparent. I have as yet had no opportunity of repeating his experiments.

The chlorides most commonly worked with, have been those formed by the solution of the hydroxide in hydrochloric acid, followed by precipitation or crystallization from concentrated hydrochloric acid.

Berzelius attempted to remove the excess of hydrochloric acid

[1] *Chem. News.*, 60, 17.

by heating the salt to 60° C. but was not able to obtain a definite compound. Two analyses gave

ZrO_2	0.332	0.485
AgCl	0.661	1.096

The silver chloride should be about two and one-third times as much as the oxide.

Paykull dried the salt between filter paper and found the composition of the crystals to be $ZrOCl_2.8H_2O$, the amorphous form precipitated by hydrochloric acid being $2ZrOCl_2.13H_2O$.

Endemann has described basic or oxychlorides $Zr_2O_4Cl_4$, ZrOClOH, and $Zr_6O_8Cl_7(OH)_9$; Troost and Hautefeuille have described others, $Zr_2O_3Cl_2$ and Zr_3OCl_6. In fact water is so easily taken up and hydrochloric acid lost that a large number of such indefinite compounds might be prepared by slightly varying the conditions.

Nylander[1] made a series of attempts at dehydrating the chloride. He prepared the chloride by dissolving the hydroxide in hydrochloric acid and evaporating to crystallization. The salt formed white needles, easily soluble in water. They were washed with alcohol and for analyses I and II were pressed between filter paper; III and IV were dried over sulphuric acid. The results were as follows:

	I.	II.	III.	IV.
Zr	27.56	25.69	30.11	31.78
Cl	21.58	21.58	23.06	23.80
Loss (H_2O)	50.86	52.78	46.83	44.12

or calculated on a dry basis:

Zr	56.08	54.41	56.63	57.18
Cl	43.02	45.59	43.37	42.82

Again preparations were made as before. I was dried between filter paper, II over sulphuric acid, III was pressed between filter paper and then dried over sulphuric acid, IV was dried a long time over sulphuric acid. The analyses gave the following:

	I.	II.	III.	IV.
Zr	28.52	34.91	37.78	35.69
Cl	21.93	26.09	25.87	21.74
Loss	49.55	39.10	36.35	42.57

or calculated on a dry basis:

Zr	56.93	57.23	59.34	62.14
Cl	43.07	42.77	40.66	37.86

Lastly he allowed a solution of the chloride to evaporate over

[1] Bidrag till kännedomen om Zirkonjord. Inaug. Diss. Lund, *1864*.

sulphuric acid washed the crystals obtained with alcohol and pressed them between filter paper. Analyses gave:

Zr	27.94	28.74
Cl	27.32	26.67
Loss	44.74	42.62

or calculated on a dry basis:

	Found			Theory.
Zr	50.56	50.04	Zr	38.50
Cl	49.44	49.96	Cl_4	61.50

The above results show that his preparations were indefinite oxychlorides or mixtures in varying proportions of zirconium tetrachloride and oxychloride.

Bailey repeatedly crystallized the chloride from hydrochloric acid, washed it with hydrochloric acid and then removed the free acid.

(1) By washing with a mixture of one part alcohol and ten parts of ether.

(2) By gently heating the salt.

(3) By exposing the finely divided salt at ordinary temperatures in a vacuous desiccator over potash until no hydrochloric acid appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid and precipitating the chlorine by means of silver nitrate. By method (2) a constant and progressive diminution of chlorine was observed. Therefore no analyses were made. For the other methods he gives the results of the analyses by a statement of the relation of ZrO_2 to AgCl.

	ZrO_2 :	AgCl
Berzelius determination	1 :	1.991
" "	1 :	2.260
Bailey's method 1	1 :	2.206
" " "	1 :	2.179
" " "	1 :	2.226
" " "	1 :	2.260
" " 2	1 :	2.264
" " " without washing	1 :	2.245
" " "	1 :	2.309
" " "	1 :	2.285
$ZrOCl_2$	1 :	2.350

These preparations are evidently mixtures also.

Hermann[1] states that the hydrated chloride, gotten in crystals on evaporating its aqueous solution, becomes opaque at 50° C., giving off part of the water and half of the hydrochloric acid and leaving a basic chloride or oxychloride, $ZrCl_4.ZrO_2.18H_2O$ or $ZrOCl_2.9H_2O$. The same compound is obtained in stellate groups of white silky prisms on evaporating a solution of the chloride. These crystals when heated become white and turbid and are converted into the anhydrous dioxychloride, $ZrCl_4.2ZrO_2$.

The conditions here are inexact and though Hermann may have obtained these compounds he would doubtless find it difficult to prepare them again. While it is perfectly true that an oxychloride is formed on the evaporation of an aqueous solution of the chloride, I have been unable to obtain the compounds he mentions. Linnemann[2] maintains that crystallization from hydrochloric acid (sp. gr. 1.17) and treatment with alcohol and ether gives a fine, crystalline, snow white, silky body, leaving fifty per cent. of its weight on ignition and therefore very nearly pure $ZrCl_4$ which should leave 52.5 per cent. He claims that this is "chiefly a neutral, not a basic compound."

My own experiments on the dehydration of this salt have extended over the past two years, as opportunity was afforded. Several series of experiments were undertaken, some along the lines attempted by others, and others by methods not tried before. In all the purified chloride obtained by repeated crystallization from hydrochloric acid was used, the salt being still wet with the excess of the acid. There was no attempt at drying this between filter paper. The method of preparing this salt has been fully described in a previous paper in the *Journal of Analytical and Applied Chemistry*, **5**, 551.

In the first experiment this chloride was washed once with water and then put in a desiccator and dried over calcium chloride (porous desiccated). It remained in the desiccator about seven months. Even after this lapse of time it still continued to show a slight loss in weight. It yielded on analysis 48.84 per cent. ZrO_2.

Another portion was placed in a jar over solid lumps of sodium hydroxide. After six weeks the loss was very slight. Careful

[1] Watts' Dict., 5, 1080.
[2] *Chem. News.*, 52, 224.

ignition left a residue of ZrO_2, equivalent to 42.99 per cent. of the original weight. There was found to be 24.44 per cent. of chlorine present.

Again a portion was placed over calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued, although it was slight. On analysis this gave ZrO_2 42.28 per cent., and Cl 24.35 per cent. Although the results in this and the experiment immediately preceding correspond fairly well, they are unsatisfactory as they point either to a mixture of chlorides or an oxychloride of very complicated formula and hence unsuited for the ultimate aim of the research.

Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear colorless solution. It contained 53.30 per cent. of ZrO_2. This corresponds very nearly to the formula $ZrCl_4$, and is altogether at variance with the results obtained by Nylander and with the assertion made by Hermann that half of the hydrochloric acid was lost over sulphuric acid.

This last experiment showed the possibility of securing pure zirconium chloride, provided the excess of hydrochloric acid could be removed. It was thought that this might be done by heating in an atmosphere of hydrochloric acid. A weighed flask was so arranged that it could be kept at a definite temperature while a stream of dry hydrogen chloride was passing through it. The temperature ranged from 100° to 110° C., and the chloride placed in the flask melted, solidifying again after the loss of the water and excess of hydrochloric acid. If the drying was done slowly enough, fine crystals of zirconium chloride were gotten which lost no further weight on being kept at 100° C. A

more rapid drying left a hard white mass which was quite hygroscopic. Heating this mass for several days did not cause any diminution in weight, provided the flask was kept full of hydrogen chloride. If the mass was heated even a short time in the absence of hydrogen chloride then further heating caused a continuous loss of weight even in the presence of a rapid stream of hydrogen chloride. After this it was impossible to secure a constant weight.

This method of drying has been tried repeatedly on various preparations and I regard the facts stated above as showing conclusively that a neutral zirconium chloride can be prepared and dried.

Analyses of this chloride gave the following percentages of ZrO_2:

52.70 52.78 52.63

Experiments have already been begun with a view of utilizing this body in a series of experiments looking to a revision of the atomic weight of zirconium.

In connection with this subject it may be well to mention some improvements in the method of purifying zirconium chloride. (See *Journal of Analytical and Applied Chemistry*, **5**, 551.)

In the first place the separation from silica by evaporation to dryness is not complete. It is impossible to heat this chloride to the necessary temperature without such a decomposition as will render the zirconium chloride also insoluble. It is best then to make this separation as thorough as possible by heating, then to change the chloride into oxide by ignition and to treat this several times with hydrofluoric acid until the trace of silica is all driven off. This silica is too small in amount to interfere with ordinary uses but would have to be removed where perfect purity was demanded.

Again where the hydroxide is dissolved in dilute hydrochloric acid, or contained so much water that the acid was greatly diluted by it, it will be found that more or less of a white insoluble powder will form on evaporating, as recommended on a water-bath, and on subsequent treatment with boiling strong hydrochloric acid. By a careful arrangement of glass wool in a hot-water funnel the dissolved chloride can be filtered away from

this insoluble mass. It seems to be quite insoluble in hydrochloric acid though easily dissolved by water. Analysis shows that this mass is $ZrOCl_2$ and with it was found, as an impurity, whatever silica the separation by heating failed to remove.

Lastly, my assistant, Mr. Baskerville, has shown that much time and hydrochloric acid will be saved if, in the solutions containing much iron, the zirconium hydroxide be first precipitated out by means of sulphur dioxide. This precipitate can then be dissolved in acid and purified by crystallization as already recommended.

Of course it need scarcely be mentioned that if silica has been removed by ignition and treatment with hydrofluoric acid, it will be necessary to fuse once more with caustic alkali and repeat the ordinary purification.

UNIVERSITY OF NORTH CAROLINA,
April 12, 1894.

SEPARATION OF ZIRCONIUM BY MEANS OF SULPHUROUS ACID.

BY CHARLES BASKERVILLE.

Received April 16, 1894.

WHILE testing the accuracy of the various methods recommended for the estimation of zirconium I was led, because of the analogy of the elements, to try a method commonly used with titanium; *viz.*, prolonged boiling of a potassium bisulphate fusion in dilute solution with sulphurous acid in excess. On application of this method, however, on a solution of zirconium sulphate (prepared by dissolving the hydroxide in sulphuric acid), I failed even after boiling four hours with an excess of sulphur dioxide to obtain a precipitate, if the solution was acid. If the solution was nearly neutralized with ammonium hydroxide and then boiled with an excess of sulphur dioxide, after being greatly diluted, a precipitate was produced. This precipitation, however, was incomplete, even after boiling six hours or passing steam through the same for two or three hours. The precipitate too was very finely divided, running through all filter papers at my command. Therefore this method could not be used.

But an addition of sulphurous acid to a solution of zirconium chloride, even in a cold acid solution, a dense white precipitate was immediately noted. On boiling with an excess of sulphurous

acid in a neutralized solution, *i. e.*, the hydrochloric acid solution neutralized by ammonium hydroxide until the slight precipitate formed was no longer dissolved on boiling, and this precipitate then taken up with two or three drops of dilute hydrochloric acid, the zirconium was completely precipitated.

The accuracy of the method is seen in the following results:

	Found.	Used.
ZrO_2	0.1074	0.1077
"	0.1078	0.1077
"	0.1043	0.1038
"	0.1070	0.1077
"	0.1047	0.1050

The precipitation took place immediately on addition of sulphurous acid, and after two minutes boiling the precipitate settled quickly and was easily filtered.

This method then is applicable to the chloride only, and a sulphate would have to be first changed into chloride by precipitation with ammonium hydroxide and re-solution in hydrochloric acid. The presence of large amounts of such salts as ammonium chloride did not aid the precipitation of the sulphate. The presence of free hydrochloric acid must be avoided and it is best to use a fresh solution of sulphurous acid or the sulphur dioxide gas direct.

This method affords an excellent means of separating zirconium from iron. Several experiments were carried out upon solutions containing known amounts of the chlorides of these two metals. The zirconia was precipitated by sulphurous acid, boiled five minutes, and washed four or five times with hot water. The iron was titrated in the filtrate.

The experiments resulted as follows:

	Found.	Used.
ZrO_2	0.1074	0.1070
Fe	0.0825	0.0823
ZrO_2	0.1078	0.1070
Fe	0.0820	0.0823
ZrO_2	0.1043	0.1043
Fe	0.0439	0.0423

This method served for the separation of zirconium and aluminum as well, as may be seen by the following results:

	Found.	Used.
ZrO_2	0.1042	0.1043
Al_2O_3	0.0608	0.0610
ZrO_2	0.1070	0.1070
Al_2O_3	9.0316	0.0305

UNIVERSITY OF NORTH CAROLINA.

ON THE ANALYTICAL PROPERTIES OF IRON PHOSPHIDE AND PHOSPHATE.

By L. M. Dennis and B. S. Cushman.

Received May 17, 1894.

IN the year 1886, Cheever, in an article in the *Transactions of the American Institute of Mining Engineers*, **15**, 448, sought to explain the variation in effect of a definite amount of phosphorus upon the properties of iron and steel by assuming that the phosphorus exists in the metal in two conditions; *viz.*, as phosphide, which is harmful, and as phosphate, which is harmless, or comparatively so. To demonstrate this he used the following method:

"A weighed sample of iron is treated in the cold with a solution of the double chloride of copper and ammonium until the iron is all dissolved, then filtered without washing. The residue of copper, carbon, phosphorus, etc., is next digested at 50° C. for two hours with 100 cc. of a saturated solution of ammonium oxalate, then filtered and washed; the filtrate contains the phosphate of iron; the residue the phosphide."

Later, in the same article, he shortens the method as follows:

"The copper, carbon, phosphorus, etc., residue is shaken in a flask for five minutes with seventy-five cc. of a cold, one per cent. solution of hydrochloric acid (two cc. strong hydrochloric acid to 100 cc. water—free from chlorine), then filtered and washed with water, the filtrate made strongly acid with nitric acid and evaporated nearly to dryness, and the phosphorus precipitated by molybdate solution."

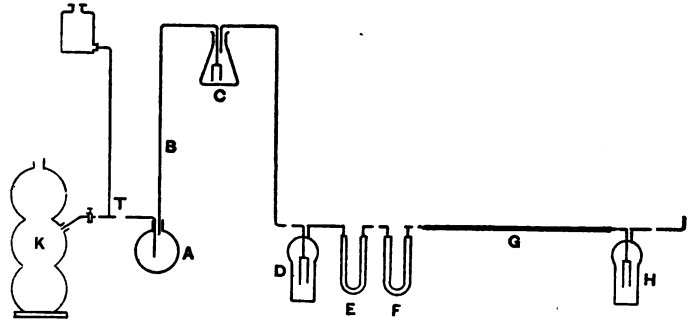
In a second paper in the same Journal, **16**, 269, Cheever gives results obtained by another method, he here volatilizing the iron as chloride by chlorine, "and analyzing the residue for phosphorus, which, if present, must be in the form of phosphoric acid; for the iron phosphide would be volatilized."

At that time doubt was cast upon the accuracy of Cheever's work because of the uncertainty as to the behavior of phosphide of iron towards the different reagents which he employed. In the hope of removing some of that uncertainty the authors entered upon the experimental work detailed below.

Preliminary work upon the phosphides of iron carried out by Mr. Russell Elliott in this laboratory in 1891-2, seemed to show that the different phosphides, of which, according to Freese,[1] there are three, Fe_2P_4, FeP, and Fe_2P, behave quite similarly towards various solvents. For this reason, and also because of the length of time required for the preparation of a pure sample, we prepared and examined only one of the phosphides, selecting that which is formed by treating anhydrous ferrous chloride with phosphine at a red heat.

Ferrous Chloride.—The purest piano wire obtainable was placed in a combustion tube, which was connected on one side with an apparatus furnishing dry hydrochloric acid gas, and on the other side with a Schiff nitrometer[2] filled with strong potassium hydroxide solution. When the air in the tube had been completely displaced by the hydrochloric acid gas, as was shown by the complete absorption of the gas by the caustic potash solution, the combustion tube was heated to redness. The ferrous chloride produced was partly in the form of glistening light-yellow plates, and partly a yellowish amorphous powder. Careful tests showed that it was completely free from ferric chloride.

Phosphine.—The phosphine was generated by the action of a solution of potassium hydroxide upon phosphorus. The form of apparatus finally adopted has given such satisfactory results that a brief description of it may not be out of place. It consists of:



1. The 500 cc. distilling flask A in which the phosphine is generated.

[1] *Pogg. Ann.*, 132, 225.
[2] *Ztschr. anal. Chem.*, 7, 430.

2. The upright tube B which serves as a condenser, and which is widened after entering the cooling flask C to prevent its becoming clogged by the condensation of the phosphorus.

3. The cooling flask C which is surrounded with ice-water.

4. The wash-bottle D.

5. The two U tubes, E and F, filled with calcium chloride for drying the gas.

6. The combustion tube G.

7. The wash-bottle H which prevents the air from diffusing back into the combustion tube.

8. A Kipp apparatus, K, for generating hydrogen.

9. The ⊥ tube T, through which water could be driven into A from the reservoir above in order to stop the generation of the phosphine by diluting the caustic potash solution.

The most uniform evolution of phosphine was obtained by using a 1:1 solution of potassium hydroxide, a stronger solution causing a more rapid generation of the gas than was desirable. Although the phosphine resulting from the use of this moderately concentrated caustic potash was not as pure as that obtained with a very concentrated solution,[1] yet the phosphide obtained was probably not influenced to any great extent by the small amounts of hydrogen given off early in the phosphine evolution. The hydrogen would reduce some of the ferrous chloride to metallic iron, but if we accept the statement of Freese,[2] the product is the same whether phosphine acts upon anhydrous ferrous chloride or upon metallic iron. To avoid, however, the production of any unnecessarily large amount of hydrogen the contents of the generating flask was at no time heated to boiling, this precaution serving to lessen the amount of hydrogen arising from the secondary reaction between the potassium hydroxide and potassium hypophosphite:

$$KH_2PO_2 + 2KOH = K_3PO_4 + 2H_2.$$

It was thought that the hydrogen thus set free might reduce the phosphide after the latter had formed, but later experiments with the pure phosphide showed that it was not reduced when highly heated in a current of hydrogen. The solution of potassium hydroxide should be cooled before being poured upon the

[1] A. W. Hofmann, *Ber. d. Chem. Ges.*, 1871, 200.

[2] *Pogg. Ann.*, 132, 225.

phosphorus in the flask, in order to avoid the immediate generation of any phosphine, as that would cause an explosion upon coming in contact with the air in the flask. As soon as all connections had been made, hydrogen from the Kipp generator was run through the apparatus until all air had been expelled. The sand-bath under the generating flask was then gently heated until the phosphine began to come off somewhat rapidly. The hydrogen was then shut off and the flame removed, the latter being replaced only when the solution of the gas had nearly ceased. This procedure greatly lengthened the duration of the current of phosphine.

When nearly all of the hydrogen had been driven from the apparatus the phosphine burst into flame at the end of the outlet tube. The combustion tube was then heated. As soon as the hydrochloric acid gas, formed by the action of the phosphine upon the ferrous chlorine, began to come off, the flame at the outlet tube ceased to burn. The ferrous chloride gradually darkened, and after half an hour, when the reaction was completed, it had assumed a dark bluish-gray color.

Upon breaking the tube there was found a brittle, porous substance which rarely showed any crystalline structure. It was powdered in an agate mortar, then digested with hot hydrochloric acid (1 : 12) until it was not at all attracted by the magnet, and was finally dried over sulphuric acid in an atmosphere of carbon dioxide.

Analysis of the Phosphide.—Stöckmann[1] states that he always obtained too low results for phosphorus when aqua regia was used as a solvent for spiegeleisen. He also tested the gases which were given off when the sample was dissolved, by passing them through an oxidizing medium, and in each case was able to detect phosphorus in them. For this reason we first tried other solvents, but although the phosphide was quite strongly attacked by nitric acid and by hydrochloric acid, and especially by nitric acid to which potassium chlorate was gradually added in small amounts, complete solution was in no case effected even by several hours treatment.

Portions of the phosphide were then treated with aqua regia in a small flask to which a return-flow condenser was attached.

[1] *Ztschr. anal. Chem.*, 16, 175.

After passing through the condenser the escaping gases were passed through a Mitscherlich bulb containing a solution of potassium hydroxide which had previously been saturated by chlorine. After the phosphide had been completely dissolved, the potassium hydroxide solution was acidified with nitric acid and was repeatedly evaporated with nitric acid until all chlorine had been expelled. Ammonium molybdate was then added, but no trace of a precipitate resulted. Aqua regia was, therefore, adopted as the solvent for the phosphide.

The following method of analysis was first tried:

About 0.1 gram of the phosphide was dissolved in aqua regia (one part of nitric acid to three parts of hydrochloric acid), and the solution, after being diluted, was precipitated by ammonium hydroxide. An excess of ammonium sulphide was then added to break down the ferric phosphate, and the solution was kept at 70° C. for fifteen hours. The ferrous sulphide was then filtered off, dissolved in dilute hydrochloric acid, and the iron then oxidized by bromine water. Upon precipitating this solution with ammonium hydroxide and weighing the iron as ferric oxide, too high results were obtained since the precipitate was found to contain phosphoric acid.

The method finally adopted for the analysis of the phosphide was as follows:

The sample was dissolved in aqua regia, the solution repeatedly evaporated with nitric acid, and the phosphoric acid determined by the molybdate-magnesia method. To determine the iron in the filtrate from the ammonium phosphomolybdate precipitate, the method of W. H. Krug[1] was used with satisfactory results. The iron was precipitated in the cold with ammonium hydroxide, and the ferric hydroxide, after thorough washing, was dissolved in nitric acid and again precipitated from the cold solution with ammonium hydroxide. After washing until all chlorides had been removed, the iron was weighed as Fe_2O_3.

The results obtained were as follows:

	Found.	Calculated for Fe_3P_4	Calculated for FeP
Fe	64.21	57.52	64.36
P	35.62	42.48	35.64

[1] *J. Anal. Appl. Chem.*, 5, 674.

The work of other investigators in this field had led us to expect as a product, not FeP but Fe_2P_4. Yet the constancy of composition shown by separately prepared portions of our product, its completely non-magnetic character and the agreement of the analysis with the calculated percentages, leave but little doubt as to the purity and identity of the phosphide.

The fact that the true phosphides of iron are *non-magnetic* seems to have been overlooked by recent writers, a circumstance which has probably led Hvoslef, Schneider, Percy, and others, to regard a mixture of phosphide of iron and iron (they give it the formula Fe_3P) as a definite phosphide. Howe[1] cites the work of Hvoslef and Percy, and says: "These facts suggest that iron and phosphorus preferentially combine in this particular ratio." But he does not mention the careful and extended researches of Freese upon this subject, who says:[2] "Endlich habe ich versucht, das von Hvoslef beschriebene Phosphoreisen Fe_3P, welches derselbe durch Glühen des Phosphorets FeP unter einer Decke von Borax erhalten haben will, darzustellen, allein bis jetzt vergeblich." After describing some of his own experiments, made according to Hvoslef's method, Freese concludes: "Hieraus schliesse ich, dass Hvoslef's Phosphoreisen nur ein Gemenge von Eisen mit Phosphoreisen ist, denn stets fand ich bei einem anerkannt reinen Eisenphosphoret den nach längerer Behandlung mit heisser Chlorwasserstoff saüre verbliebenen Rückstand mit dem Phosphoret gleich zusammengesetzt."

Ferric Pyrophosphate.—This salt was chosen as representing perhaps more nearly than any other the condition of the oxidized phosphorus in iron and steel. A sample of the pure ferric pyrophosphate was heated for half an hour over the full Bunsen flame: it retained its yellow color and was completely soluble in concentrated hydrochloric acid.

Experiments with Solvents.—Before attempting to separate the phosphide of iron from the pyrophosphate in samples of iron or steel, it was necessary to find a solvent which would completely dissolve the pyrophosphate and leave the phosphide unattacked. The reagents tried were solutions of ammonium oxalate, potassium oxalate, ammonium citrate, ammonium carbonate, ammo-

1 Metallurgy of Steel, p. 55.
2 *Pogg. Ann.*, 132, 262.

nium cupric chloride, and dilute solutions of chromic, sulphuric, nitric, and hydrochloric acids; both rapid boiling and long digestion at 100° C. were employed. Clear solutions of the pyrophosphate were obtained only with ammonium oxalate, ammonium citrate, and hydrochloric acid. Portions of fifty milligrams of the pyrophosphate were then digested on a hot plate with 100 cc. of each of these three solvents. Complete solution resulted

with hydrochloric acid (1 : 1)..... in 2 minutes
" ammonium oxalate (concentrated).. " 45 "
" " citrate (sp. gr. 1.09) " 90 "

On diluting the ammonium oxalate solution with water a white precipitate resulted, and as this could be dissolved only by adding hydrochloric acid and boiling, the use of ammonium oxalate was abandoned.

One hundred milligram portions of the phosphide were then treated with hydrochloric acid and ammonium citrate under the same conditions as were required for the complete solution of the pyrophosphate. The residues were collected on counterpoised filters, dried, and weighed. It was found that the phosphide which had been digested with hydrochloric acid had lost about four per cent. of its weight. The filtrate from this portion, after the hydrochloric acid had been expelled by evaporation with nitric acid, gave strong tests for both iron and phosphorus. The sample of phosphide which had been digested with ammonium citrate showed no appreciable loss of weight, and hence a solution of this reagent, of a sp. gr. of 1.09, was used in the following experiments upon the separation of the pyrophosphate of iron, and phosphide of iron, in samples of iron and steel.

Before trying the ammonium citrate solution a preliminary experiment was made to ascertain the nature of the action of hydrochloric acid (1 : 1) upon the phosphorus in iron. A sample of pig iron, containing 0.205 per cent. total phosphorus, was treated with the acid until all action had ceased. The solution was filtered, the filtrate evaporated with nitric acid, and the phosphorus determined by the molybdate-magnesia method. Two determinations gave 0.153 and 0.154 per cent. phosphorus. The determination of the phosphorus in the unattacked residue showed that only 0.008 per cent. remained behind, from which

it follows that over twenty per cent. of the phosphorus present escaped in gaseous form during the solution of the iron.

The ammonium citrate separation was then tried on two samples of steel to ascertain whether the method would give agreeing results. The sample should be as finely divided as possible, and for this reason filings were used in the following determinations:

Five grams of "Open Hearth" steel was digested on a hot plate (100°), with ammonium citrate solution, for an hour and a half. The solution was then filtered through asbestos. The residue was thoroughly washed with water, dissolved in nitric acid (1.20 sp. gr.), and the phosphorus determined by the molybdate-magnesia method.

Total phosphorus in the sample was 0.044 per cent.

Phosphorus in the residue after treatment with ammonium citrate, 0.033 and 0.032 per cent.

A sample of Bessemer steel, containing 0.107 per cent. total phosphorus, gave by the same method 0.046 and 0.053 per cent. of phosphorus in the residue.

No further analyses of iron or steel samples were made, for our object in taking up the work was not the investigation of the condition of phosphorus in samples of commercial products, but was merely to attempt to devise a method to separate phosphide of iron from pyrophosphate.

The chlorine method employed by Cheever was also tried on the phosphide and pyrophosphate.

Eighty milligrams of the phosphide were heated in a current of dry chlorine. As the temperature rose sparks shot out from the surface of the phosphide. At a low red heat a glow ran through the substance which then melted and volatilized completely in a few minutes.

A sample of the ferric pyrophosphate was then heated for half an hour in a current of chlorine at the highest temperature obtainable by the use of a combustion furnace, but no loss in weight resulted.

A mixture of 0.0435 gram of the pyrophosphate, with 0.0292 gram of the phosphide, was then heated in chlorine in the same manner. The residue in the boat weighed only 0.0231 gram. As this seemed to indicate that in the volatilization the phos-

phide exerts some reducing action on the pyrophosphate, causing a volatilization of some of the constituents of the latter compound, another experiment was tried with a mixture containing a slightly higher per cent. of phosphide, to see whether there would be a correspondingly greater loss in the pyrophosphate.

0.0561 gram of the pyrophosphate, and 0.0472 gram of the phosphide, treated with chlorine, gave a residue weighing 0.0193 gram, a result which seems to sustain the above supposition.

CORNELL UNIVERSITY,
May, 1894.

NOTES ON ALUMINUM.[1]

BY GEORGE FREDERICK ANDREWS.

THE writer of this paper has made a large number of experiments with aluminum particularly with reference to its use in jewelry etc. The facts stated are the results of some of these experiments.

Alloys containing Gold.—The alloys of gold and aluminum are interesting, though of little practical use except for decorative purposes. The alloy with six per cent. of gold is as white as pure aluminum but much more brittle. The alloy with ten per cent. of gold is harder than aluminum but does not work well, except at a high temperature. Its color is light violet-brown. The alloy with fifteen per cent. of gold is a very soft fine-grained metal. It has a slight violet tint, although nearly white. The alloy with fifty per cent. of gold has a beautiful violet color. It is very soft and spongy. The alloy with seventy-eight per cent. of gold is very brittle. The color is peculiar; it is between pink and violet. The alloy with ninety per cent. of gold has a pale violet color, while the alloy with ninety-four per cent. of gold has a color approaching pink again. Alloys containing small percentages of aluminum leave a bright violet color on the cupel, under the blowpipe.

An alloy containing fifty per cent. of gold, forty-five per cent. of copper, and five per cent. of aluminum takes the color and polish of fourteen carat gold but easily tarnishes. This alloy has also been used in electroplating, but it is not entirely satisfactory for this purpose.

Alloys containing Silver.—Alloys containing from four to eight

[1] Abstract from a paper read before the Rhode Island Section, February 15, 1894.

per cent. of silver, and from ninety-six to ninety-two per cent. of aluminum are useful for many purposes. They are harder than aluminum but not brittle. They take a very fine polish and hold it well. Their color is very near that of fine silver. These alloys are now used for the manufacture of charms, medals, metal trimmings and decorations of various kinds.

Alloys containing Nickel.—The alloy containing fifty per cent. of nickel and fifty per cent. of aluminum, has a dull gray color. It is very porous and so brittle as to be useless.

The following alloys of copper, nickel and aluminum are all very hard, fine-grained and show great strength. The alloy containing sixty-six per cent. of copper, twenty-four per cent. of nickel and ten per cent. of aluminum takes a fine polish and has the color of ten carat gold. The alloy containing fifty-five per cent. of copper, thirty-three per cent. of nickel and twelve per cent. of aluminum, has a beautiful golden-brown color. The alloy containing 72½ per cent. of copper, 21¼ per cent. of nickel and 6¼ per cent. of aluminum closely resembles it, but the color of the latter is richer and deeper. These alloys may become very useful for decorative purposes.

Solder for Aluminum.—Notwithstanding the assertions which are still heard to the contrary, aluminum can be successfully soldered. The writer has used solder which makes a clean, perfectly firm joint, and is in every way satisfactory. It requires no "soldering fluid" and no soldering iron.

Melting of Aluminum.—In melting aluminum the temperature should be kept even and not much above the melting point of the metal. The metal should be fed into the crucible in small pieces and pushed down as fast as it becomes soft. The most serviceable flux is a little tallow, although it is not necessary to use any. A sand crucible must not be used as the aluminum readily attacks the silicon.

In alloying, the aluminum should be put into the crucible after the other metal or metals have become liquid.

Restoration of the Mat.—Aluminum can be cleaned, and its peculiar mat restored by dipping for a minute and a quarter, in a solution of three ounces of caustic potash in a quart of water, then washing thoroughly and dipping in a mixture of three parts nitric, and two parts sulphuric acid, by volume.

Caustic soda can be used with nearly as good results. The main advantage in the substitution is the lower price of caustic soda.

LABORATORY OF CORNELL AND ANDREWS.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.

BY WALTER D. FIELD.

(*Continued from Vol. 15, p. 140.*)
Received September 12, 1893.

PART II.

NITRATION OF THE FIBER.

MIXED cotton and flax fiber in the form of paper, from two to three one-thousandths of an inch thick and cut into one inch squares, is nitrated by the Celluloid Manufacturing Company, and the same paper, left in long strips, one inch wide, is used for nitration by the Zylonite Manufacturing Company, of North Adams, Mass. The Celluloid Manufacturing Company introduce the cut paper into the mixed acid by means of the arrangement shown in Fig. 1, H, which is a rapidly revolving,

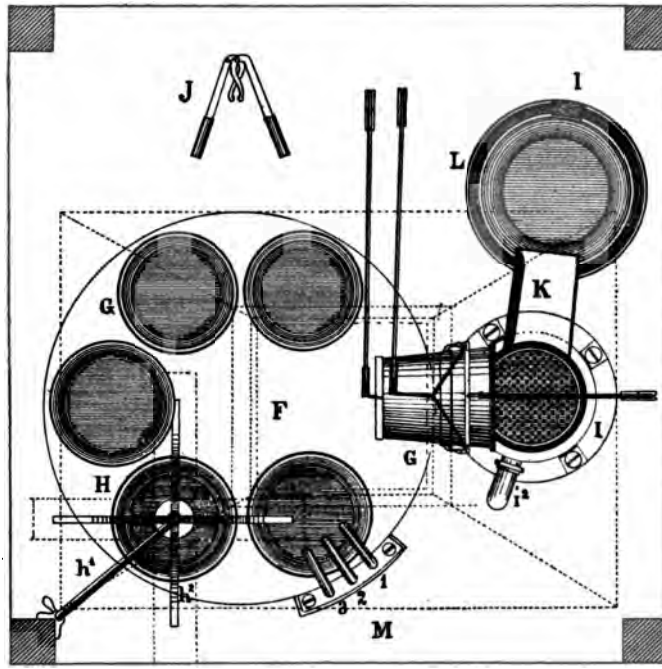


FIG. 1.

hollow tube, flared at the lower end, and immersed in the mixed acid. The centrifugal force of the revolving tube throws the paper towards the sides of the vessel G, leaving the center of the vessel ready for fresh paper. The Zylonite Manufacturing Company simply cut the paper into long strips and introduced it into the mixed acids by means of forks. The arrangement used by this company for holding the mixed acids was a cylindrical vessel divided into a number of sections, the whole revolving like a turntable, thus allowing the workman to nitrate successively each lot of paper at a given point. This company did not remove the acid from the paper after its immersion, but plunged it immediately into the water, thus losing a large proportion of acid. The Celluloid Company, on the other hand, by using the paper in smaller pieces, using more paper to a pound of acid, and wringing the mixed acid from the paper before immersion, had by much, the best process of nitration. Their method of separating the acid and paper will be seen in Figs. 1 and 2, G and I.

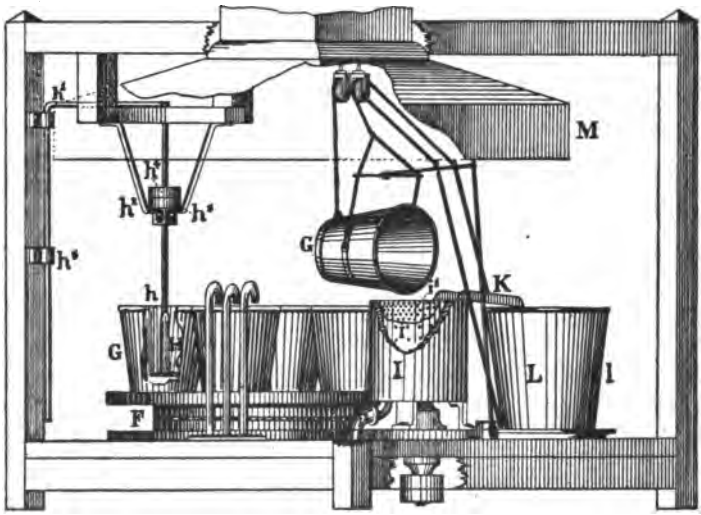


FIG. 2.

The other manufacturers of pyroxylin use earthenware vessels and glass or steel rods, hooked at one end, having small pieces of rubber hose pulled over the other end to prevent the hand from slipping. The form of vessel in general use is that given

in Fig. 3. It is sufficient in size to nitrate one pound of cotton.

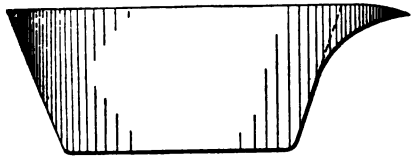
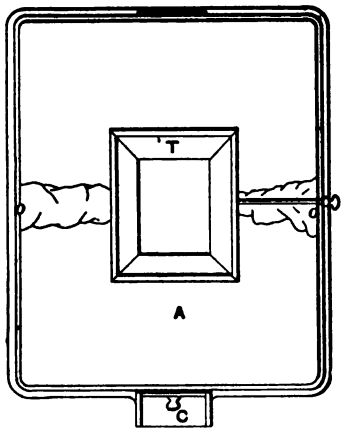


FIG. 3.

The hook on one end of the rod enables the workmen to pull the pyroxylin apart and thus insures saturation of the fiber.

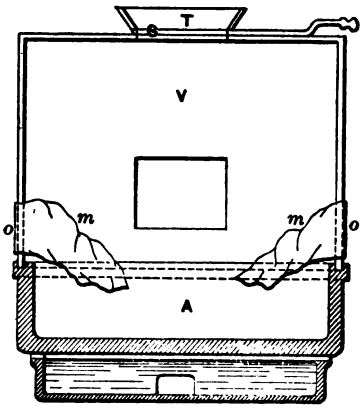
The nitrating apparatus of Tribouillet and de Besaucele (Eng. Pat., No. 5,057, 1878; Ger. Pat., No. 6,828, 1879) is given by both Bockman (Das Celluloid, 1888) and Heinzerling (Die Fabrikation Kautschuk and Guttapercha Waaren, 1883), and it is the only apparatus they mention, although Hyatt's apparatus was then in use. The plans for this nitrating box have been reproduced in Figs. 4 and 5. It is of a very unhandy construction and any workman using it would soon discard the hood V as unnecessary. The rubber sleeves would only be in his way and the acid would rot them out in a very short time.

FIG. 4.



PLAN.

FIG. 5.



SECTION.

In working by hand, at the present time, it is customary to protect the workmen from the fumes of the acid by means of a hood which is being constantly exhausted by a powerful fan or blower. They are furnished with gauntlet gloves made of white rubber, and also aprons of the same material. In the winter season the room in which the nitrating is done must be kept at a tem-

perature of about 70° F., in order to secure equality in the batches.

The nitrating apparatus of White and Schupphous (U. S. P., No. 418,237, 1889) is both novel and excellent in its general plan. The cage B (Fig. 6), with its central perforated cylinder B' (Fig. 7), is intended to insure the rapid and perfect saturation of the tissue paper used for nitrating. The patentees say that no stirring is required with their apparatus. This might be true when paper is used, or even cotton, when the temperature of nitration is from 30° to 35° C., but would not be true if the temperature were raised to 50° or 55° C. In carrying out their process they proceed as follows: The paper is nitrated in the cage B, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the internal cylinder B'. After nitration the cage is carried to the wringer E, Fig. 8, of which it forms the

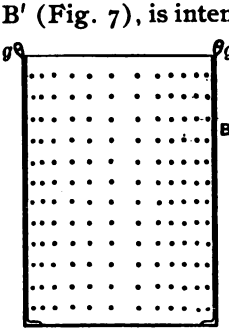


FIG. 6.

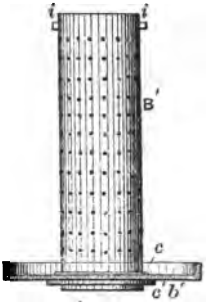


FIG. 7.

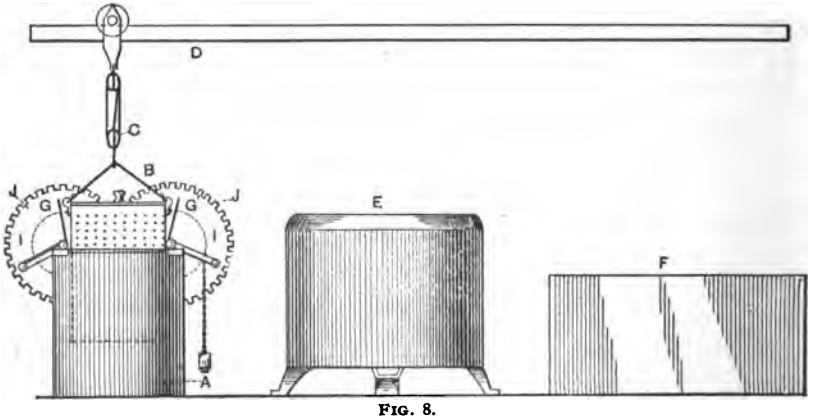


FIG. 8.

basket, and the acids removed. Finally the cage is taken to the plunge tank F where the paper is removed from the cage by simply pulling out the central perforated cylinder B'. Fig. 9, shows the nitrating pot with its automatic cover. The plunge tank F is shown in section and plan in Fig. 10. This appara-

tus is given in detail because it is the only patented method that seems to be suitable for the nitration of cotton fiber in bulk at high or low temperatures.

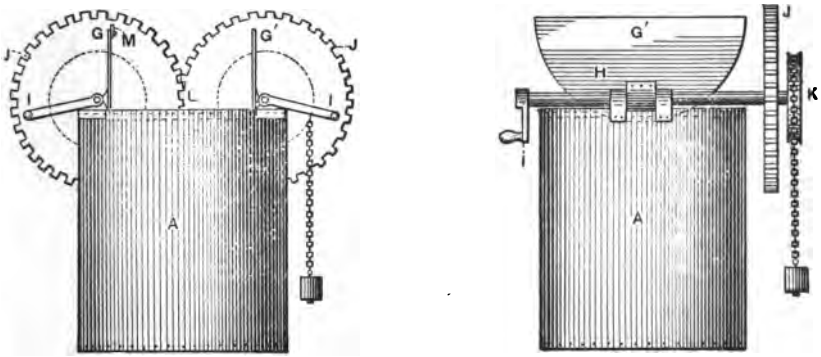


FIG. 9.

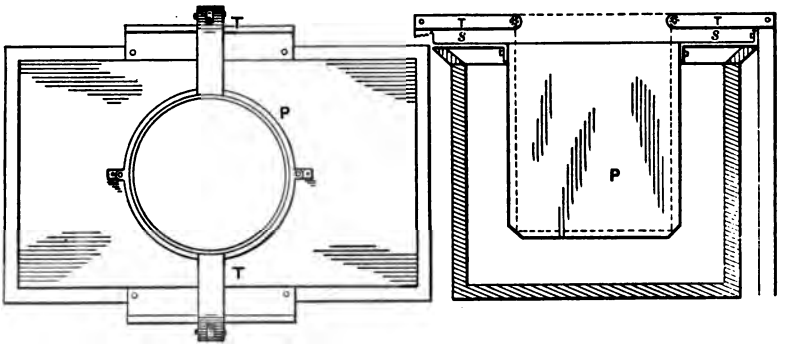


FIG. 10.

We now come to what is probably the most elaborate method of nitrating yet suggested—that is, the method patented by Mowbray, August 12, 1890 (U. S. P., No. 434,287), by which he proposes to nitrate paper in continuous lengths. The method is as yet untried. The paper loops shown in the sectional drawing (Fig. 11) are merely theoretical, for the paper web would not maintain any such position, but would settle down in the bottom of the acid tank. He allows the paper web to remain in the nitrating, or acid tank (15), from twelve to twenty minutes, then as the first part of the paper web is drawn forward, a fresh portion takes its place. One of the great problems in such an operation is how to maintain the strength of acid required in the nitrating

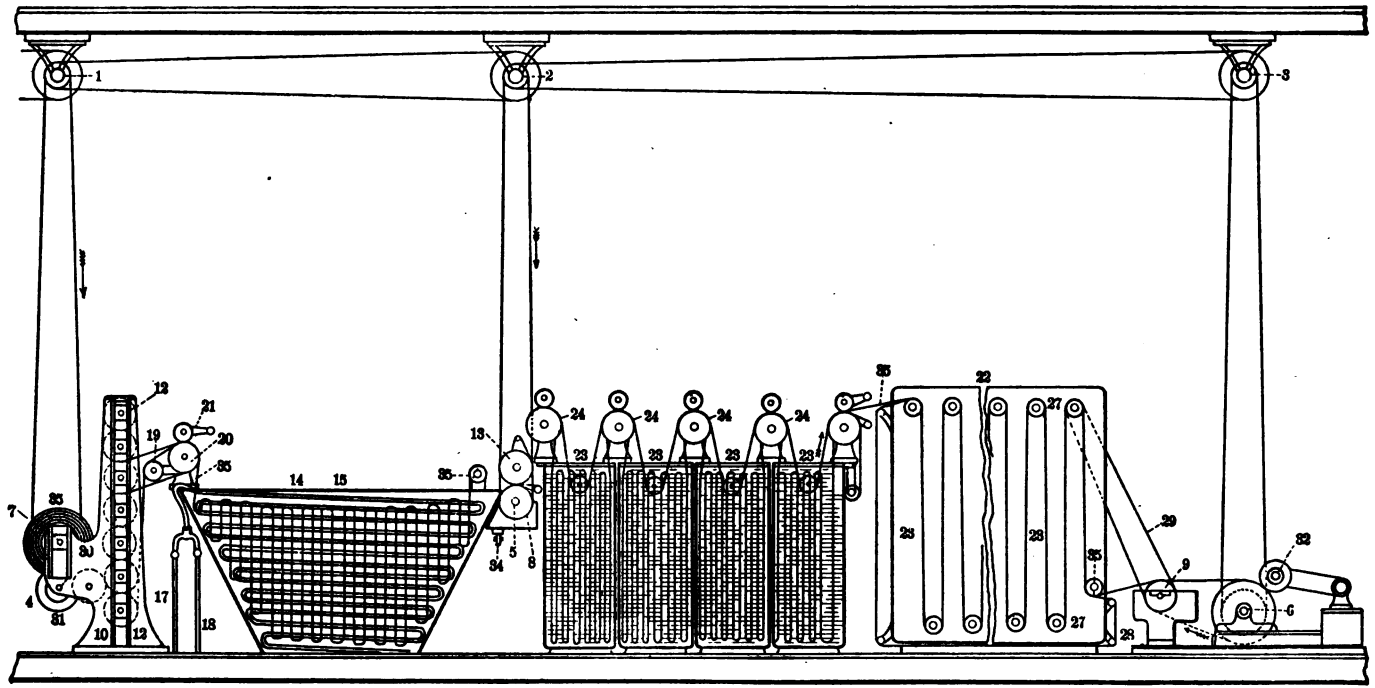

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FIG. II.

tank. Mowbray claims to be able to do this by using the methods described by him in U. S. P., Nos. 350,497, and 350,498. Such a method as Mowbray describes is certainly no better than that of Hyatt (210,611).

The best material from which to construct the various tanks required for storing the acids for nitrating vessels and for other things is, undoubtedly, steel. Mowbray, in his patent No. 350,489, 1886, claims "the use of homogeneous metal, otherwise called 'Bessemer steel' plates, for tanks, to serve as containing vessels for the mixed acids used in the process of converting cellulose into nitrocellulose." He also claims "the use of steeled cast-iron pots for holding the mixed acids, in which the cellulose is immersed during the process of conversion." Mowbray says, in the same patent: "I have discovered that cast-iron vessels treated so as to diminish the carbon therein (by exposure to continued heating, surrounded by infusoria, or iron peroxide), can be successfully used for this purpose, and that the action of acids upon metals forms a ferric sulphate which, being insoluble in the mixed nitric and sulphuric acid used, does not injuriously affect the product."

One way of constructing the vessel for holding the waste acids from the nitrating pots can be seen in Fig. 12. The inside vessel, A, is of earthenware, and may have a capacity of from 100 to 500 gallons, according to necessity. The outside vessel is of boiler steel with a flanged top, E, F. The pipe D is connected with the compressed air, and the pipe C conducts the acid as it is forced out to the desired place. It is a construction that prevents any accidents when moving the acids from place to place.

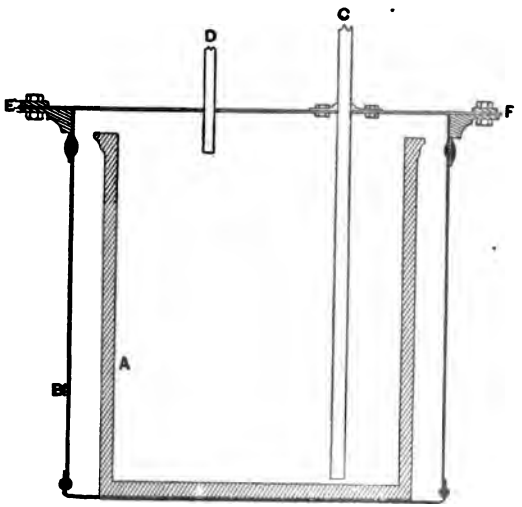


FIG. 12.

Hyatt, in U. S. P., No. 299,388, a patent for a combination of tanks so arranged as to allow of the convenient handling of the mixed acids, simply says in regard to the construction of the tanks: "We prefer to construct our tanks of wrought iron, and protect them from the corrosive action of the acids by acid-proof coatings." Steel drums will hold the mixed acids so long as they are closed from the air, but if air is allowed to enter, the sulphuric acid in the mixed acids takes up the moisture in the air, are reduced in strength at the surface, and soon begin to eat the iron or steel away. There is some choice, perhaps, in the steel to be used for such a purpose, but wrought iron is as good as steel if the air is carefully excluded from the tank. All the plants and arrangements of tanks, etc., both for nitrating and storing and using the waste acids, have been designed for an acid mixture having about the following strength:

Sulphuric acid	66 parts (absolute).
Nitric acid	17 " "
Water	17 "

the acids being used at a temperature of 30° C.

The arrangement of the plant, as described by Mowbray in U. S. P., No. 350,496, or the arrangement described in U. S. P., No. 299,388, by Hyatt, Pool, Everding, Stevens, and Wood, could not be used were the acid mixture in use of the following composition:

Sulphuric acid	62 parts (absolute).
Nitric acid	24 " "
Water	14 "

and using a temperature of 60° C. for immersion.

The nitrating apparatus of Schupphous, Mowbray, and Hyatt, were all designed for use with tissue paper as the cellulose material. The design of Schupphous might be used for cotton at low temperatures, but would be inconvenient on account of the length of time (five or six hours) required for nitrating at low temperatures.

Thus it is apparent that both the cellulose material and the method of nitrating control the construction of the nitrating plant. No plant has yet been designed for nitrating cotton fiber in its natural form at high temperatures, and using more than one pound of cotton at an immersion.

The Acid Mixture.—Many formulas have been published for producing soluble nitrocellulose. Few of them give detail enough to make them available for practical working. In many instances, although the observations were correct for the single experiment, a dozen experiments would have produced a dozen different products. Some formulas give no temperature for the immersion, others neglect even to give any specific gravities for the acids, and rather than attempt to utilize any published formula, it would be much better to spend months working out a new one to one's own satisfaction and instruction.

In the last five years, the manufacture of a pyroxylin that is almost the equivalent of the collodion cotton, has enormously increased, by reason of its use in the manufacture of pyroxylin varnishes and transparent films for photographic plates.

At the present time not more than three different formulas are in use by the manufacturers of soluble nitrocellulose in this country. The one used by the celluloid manufacturers, another in which the cotton is nitrated at high temperatures, and a third in which the temperature of the immersion is low and the time of the nitration about six hours. Of the three, the best method is the last one, or the one in which the cotton is immersed at a low temperature and then the reaction allowed to proceed in pots holding from five to ten pounds of cotton.

The following formula is essentially the one in use by the celluloid manufacturers for the production of the low form of nitrated product which they use:

Sulphuric acid	66	parts by weight.
Nitric acid	17	" " "
Water	17	" " "

Temperature of the acids at the immersion, 30° C., and the time of the immersion from twenty to thirty minutes. Cellulose in the form of tissue paper about two one-thousandths of an inch thick, one pound to 100 of acid mixture.

The nitrocellulose produced by this formula is very insoluble in the compound ethers and other solvents of pyroxylin, and is seemingly only converted or gelatinized by the action of the solvent.

The next formula produces a mixture of tetra- and penta-nitrocelluloses, hardly soluble in methyl alcohol (free from

acetone), but very soluble in anhydrous compound ethers, ketones, and aldehydes.

Nitric acid, sp. gr., 1.435	8 pounds.
Sulphuric acid, sp. gr., 1.83	15¼ "

Cotton, fourteen ounces, temperature of immersion, 60° C. Time of the immersion, about forty-five minutes. The 60° of temperature is developed by mixing the acids together. The cotton is allowed to remain in the acid until it feels "short" to the rod.

We have here the temperature record for a single batch, (made in the form of bowl given in Fig. 1) during the time of the nitration. From four to five minutes were required to immerse the fourteen ounces of cotton and then the acids had risen in temperature from 60° to 65° C. In ten minutes the temperature in the upper part of the bowl was 63½° C., and in the bottom 66° C. The batch was then turned over in the bowl and in another ten minutes the temperature of the top of the cotton was 59° C.; and in the bottom 62° C.

At the end of thirty minutes the temperature of the top was still 59° C., and the bottom 60° C. During the remaining hour and ten minutes the temperature of the top of the acid ranged from 53° to 56° C., and from 64° to 67° C. in the bottom. The time of the immersion was one hour and forty minutes. The pyroxylin produced in this immersion was not a very soluble one, quite a large proportion being insoluble in compound ethers. It will be noticed that there were two periods in which the temperature in the batch rose, and two distinct reactions took place. If the temperature during the first thirty minutes has gone up to 70° C., or 4° higher than it did go, the cotton would have been finished inside of forty-five minutes, and the pyroxylin produced would have been perfectly soluble in compound anhydrous ethers. These observations have been verified a large number of times.

The table given below is a careful record which plainly shows the great variation in the time of the immersion and the temperature by seemingly very slight causes. The table extends over fourteen working days, during which time it rained four days. The formula used is that last given, except that the

specific gravity of the nitric acid is somewhat lower. The pyroxylin produced differs only from that produced by using a nitric acid of sp. gr. 1.43, in being soluble in methyl alcohol. From thirty to thirty-five pounds of pyroxylin were produced in each of the fourteen days.

Weather.	Specific gravity.		Time.				Temperature, degrees C.		Percentage.	
	Sulphuric.	Nitric.	Hours.	Minutes.	Hours.	Minutes.	From.	To.	Increase	Loss.
1. Clear	1.8380	1.4249	..	20	4	..	57°	62°	31	..
2. "	1.837	1.4249	..	20	2	..	60°	62°	18	..
3. Cloudy	1.837	1.4226	..	45	2	..	60°	62°	7	..
4. Rain	1.837	1.4200	..	20	1	20	60°	63°	0	0
5. Clear	1.8377	1.42	1	15	2	..	58°	62°	15	..
6 Rainy	1.8391	1.422	..	35	1	40	58°	62°	..	2
7. Cloudy	1.835	1.4226	..	20	..	35	62°	64°	..	10
8. Clear	1.835	1.4222	..	35	1	10	60°	62°	5	..
9. Partly clear	1.824	1.4271	..	20	1	..	50°	60°	..	3
10. " "	1.83	1.4271	..	10	..	25	58°	60°	..	10
11. Cloudy	1.832	1.425	..	10	..	50	58°	60°	8	..
12. Rainy	1.822	1.425	..	10	..	20	58°	60°	..	10
13. Partly clear	1.8378	1.4257	..	50	1	40	50°	58°	20	..
14. Cloudy	1.837	1.4257	1	56	4	40	50°	60°	16	..

A careful examination of this table will prove very instructive. The increase in yield varies from thirty-one per cent. to nothing, and the loss runs as high as ten per cent., yet it would be unjust to say that care was not taken to make the product uniform in quality.

On the days it rained there was a loss, with the exception of the fourth day when there was neither a loss nor a gain. On the days it was partly clear, as just before or after a rain, the table shows a loss in product. We can explain this fact by reason of the moisture-absorbing qualities of the cotton. On the rainy days it would absorb the moisture from the air until, when immersed in the acids, they were weakened, and the fiber dissolved more or less in the weakened acid, producing what is known as "burning" in the batch. It will also be noticed that on the days which show a loss, the time of the immersion was correspondingly short, as on the tenth, twelfth, and seventh days.

The lesson this table teaches is, that it is almost impossible to nitrate cellulose in small quantity and get uniform results when the nitration is carried on at high temperatures.

In the next table we have the condensed results from a month's work with the above formula.

Cotton (scoured, upland)	416 pounds,	12 ounces
Nitric acid, sp. gr. 1.42–1.425 water white	4,957 "	
Sulphuric acid, sp. gr. 1.83–1.837	9,803 "	
Product	513 "	6 ounces

The high temperature nitrating formula taken as the example in this article will be found to lead to a correct judgment of the working of all such formulas. The consideration of the cold nitration method I shall make the subject of a separate paper at some later date.

IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC ACID.

By Peter S. Gilchrist.

Received May 14, 1894.

IN the JOURNAL for November, 1893, I gave a brief outline of the Hacker and Gilchrist pipe columns for saving chamber space, quoting results which had then been obtained in actual working. I wish to follow this with results of much greater interest.

As stated previously, the pipe columns were added to a plant having large chambers, the first three being each 160 feet long, and consequently not so effective as in combination with short chambers, the best work being seventeen cubic feet of chamber space per one pound of sulphur per twenty-four hours, and this with Glover and Gay-Lussac towers. The ratio of chambers have an important bearing on the amount of work done in a given space.

It has long been thought that short chambers were essential to good work, repeated experiments in Europe having demonstrated this, but there has been much tardiness in adopting them.

An observer of the chamber process notices that as the gases pass from one chamber to another a greater reaction sets in, consequently followed by an increased production of sulphuric acid. The reasons for this are obvious; the vapors strike against the surfaces of the chamber ends and the sides of the connection, causing the particles forming to interact more quickly. Again,

the gases being passed through a small aperture become better mixed, and the gases are also cooled by radiation from the lead surfaces, which is an important point in manufacturing. It has been proved in chambers of 100 feet and over, that after the gases have traversed fifty to fifty-five feet of the length the acid produced falls off considerably, so by cutting off the chamber at this point we get the maximum work from the chamber.

The important point in constructing a sulphuric acid plant is to endeavor to attain these conditions throughout the process as much as is possible, and if the mere passage of the gases from one chamber to another have such visible effects, how much more so, when these conditions are very greatly improved on, as is the case when using pipe columns.

The large, moist surfaces presented by the numerous pipes upon which the gases impinge, the thorough mixing which the gases receive by coming in contact with each successive layer of pipes, and lastly, the heat generated by the reaction, consequent upon the mixing, being carried off by the cold air passing through the pipes, are conducive to a very rapid formation of sulphuric acid.

The cyclone of last August having destroyed the acid chambers of the Darlington Phosphate Company, of Darlington, S. C., I was asked to superintend the rebuilding of the same.

The original plant consisted of three chambers, having a total capacity of 129,500 cubic feet, with a small coke tower in the rear, using Johnson's mechanical fines-furnaces, with no niter recovery, making at the outside eleven tons of 50° Beaumé acid per day.

The present plant consists of four small chambers, the first only fifteen feet long, its object being to catch the dust, the second sixty feet, the third fifty feet, and the fourth forty-three feet, having a total capacity of 100,800 cubic feet, with coke tower in the rear, using the same furnaces, and no niter recovery.

Between each chamber there is a pipe column averaging 3′.10″ by 3′.5″, and 13′.6″ high, between the last chamber and the coke tower, a small pipe case 3′.0″ by 1′.10″, and 6′.0″ long.

The average work for the last eighty-one days is as follows: Pyrites burned per day, 14,304 pounds, averaging 44.6 per cent.

sulphur, two-thirds being Virginian ore, and one-third Spanish, actually yielding forty-three per cent. sulphur. This is an equivalent of 6,153 pounds of sulphur, being 16.38 cubic feet of chamber space, per one pound of sulphur, per twenty-four hours, and in the cooler months was under fifteen cubic feet.

The average yield of acid for this period was fourteen tons of 50° Beaumé acid per day, or 4.552 pounds of 50° acid, per one pound of sulphur, per twenty-four hours.

As this means an increase over the total chamber area of seven-tenths of an inch, calculated as 50° acid, one can readily appreciate the amount of work done in the system.

The average temperatures of the chambers were as follows:

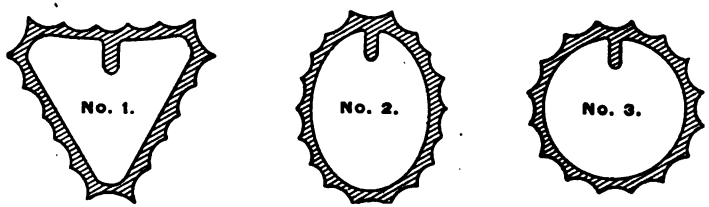
No. of chamber.	Front.	Back.
1	220° F.	222° F.
2	178° "	176° "
3	156° "	154° "
4	123° "	102° "

Atmospheric temperature, 73° F. Average oxygen in the escape gases, 6.6 per cent. Average acidity in the escape gases, 0.81 grains sulphuric anhydride per cubic foot.

The result of the application of the pipe columns over the original plant is as follows: Reduction in the size of the chambers, 21.84 per cent. Increase in the yield of sulphuric acid made, 28.18 per cent. equal to a total increase of 50.02 per cent.

Another plant is being completed in Savannah, Ga., having short chambers, pipe columns, Glover, and Gay-Lussac towers, which will, doubtless, confirm more fully the advantages of the pipe columns.

SECTIONS OF PIPES.



The construction of the pipe columns have been much improved, more especially in connection with the sections of the pipes used. The exteriors are made so as to enable the greatest amount of mixing to be got from a minimum surface of contact.

NOTE ON THE DETERMINATION OF SILICA IN BLAST-FURNACE SLAG.[1]

By P. W. Shimer, Easton, Pa.

THE object of this note is to call attention very briefly to the influence of spinel on the determination of silica in blast-furnace slags. When fluxing aluminous ores with magnesian limestone, spinel is very apt to be found in the slag, especially when the slag is basic, the alumina in this case acting as an acid and combining with part of the magnesia to form magnesium aluminate. In the determination of silica in such a slag by the method of fusion with alkaline carbonate, the spinel seems to be almost wholly unattacked by the fusion and subsequent evaporation with hydrochloric acid, and is weighed with the silica at the end of the determination. In the case of one slag, the silica, before purification, was 34.25 per cent.; after purification with sulphuric and hydrofluoric acids, it was found to be 31.52 per cent. The bluish-colored residue left after the sulphuric and hydrofluoric acid treatment was found to dissolve easily in fused potassium bisulphate, and contained alumina and magnesia in the proportions necessary to form spinel. In the case of another slag, the silica, before separation of spinel, was 39.23 per cent.; after separation, 34.73 per cent.

The points it is desired to bring out are, that spinel is not decomposed by the usual alkaline carbonate fusion and, therefore, that it is never safe to omit the treatment of the silica with sulphuric and hydrofluoric acid. All the slags in which spinel was found were stony slags and, therefore, had the usual time in which to cool and crystallize. It is quite possible that, if the same samples had been chilled, the elements of the spinel would have remained in decomposable combination with the silica. However, even in the case of chilled samples, the possible presence of minute crystals of spinel should not be ignored, especially in basic slags rich in alumina and magnesia. By successive and repeated treatment of 100 grams of a powdered spinel slag with hydrochloric and hydrofluoric acids and boiling solution of

[1] Read before the Lehigh Valley Section, May 3, 1894.

sodium carbonate in a platinum dish, it was found to be possible to separate one gram of microscopic crystals of spinel quite free from all impurities.

NEW BOOKS.

"AN INTRODUCTION TO THE ORGANIC COMPOUNDS OF EVERY-DAY LIFE." BY JULIUS T. WILLARD, M. Sc. 12mo. cloth, pp. IV; 203. Published by the author. Manhattan, Kansas. 1894. Price $1.75.

Every chemist in this country feels that anything which will tend to place organic chemistry where it belongs in our Colleges and Universities should be encouraged. It was doubtless this feeling which prompted the author to publish this little volume. The book is indeed what it pretends to be, a simple compilation. The arrangement is similar to Remsen and Bernthsen with a few changes which detract somewhat from their systematic and logical arrangement. It is on the whole so much condensed that, well-written as it is, the student must often find difficulty in following the thread connecting the various classes of compounds. The greater part of the book is devoted to the Aliphatic Series more especially to the carbohydrates. This group is neatly compiled but more appropriate for an elementary text of Applied Chemistry. Many of the every-day compounds are barely mentioned and some have been omitted entirely.

The Aromatic Series is too condensed to be of any scientific value to the student. About fifty pages are given to the derivatives of benzene proper, to naphthalene, anthracene, the terpenes, the alkaloids, the glucosides, the proteids and others. There are a good many simple facts stated, and it would seem that the book was perhaps written with the sole object of furnishing the student with these general facts.

It is, however, no longer enough that a text-book of either organic or even inorganic chemistry, be a simple mass of facts and experiments. The subject must be logically presented, leading up to, and proving new facts, by facts already known. At the same time, there must be enough assumed to develop the reasoning powers of the student and to make him feel that he is really doing the work himself. Remsen has struck the key-

note, in this respect in his "Introduction to the Study of the Compounds of Carbon" and it seems to me that it would be exceedingly difficult to place a better elementary text in the hands of the student. In fact, we are not in need of elementary text-books in organic as in inorganic chemistry. The student of organic chemistry begins with a fair knowledge of general and theoretical chemistry and a text like Bernthsen, Krafft or Richter properly used and supplemented by lectures would be far better than a small elementary book. What the organic student is most in need of is a good laboratory book, something the nature of Levy or Fischer. It is to be sincerely hoped now since organic chemistry is gaining ground in our Universities that it may not suffer from scores of poor text-books as inorganic chemistry has done.

UNIVERSITY OF MINNESOTA. G. B. FRANKFORTER.

A DETAILED COURSE OF QUALITATIVE ANALYSIS. BY ARTHUR A. NOYES pp. 80. Boston: A. D. Maclachlan, Agent, 214 Clarendon St. 1894. Price $1.

This small book of eighty pages aims to present a complete course in inorganic qualitative analysis, so arranged as to be easily followed by the student. The author follows Fresenius, in the main, as to the methods, but has modified them in some particulars. The book is divided into two parts; *viz.*, a clear, concise description of the procedure of the analysis, followed by a series of notes of explanation upon the process.

The main feature of the book, is these explanatory notes. In these the author has sought to instruct the student in all the precautions to be taken to insure accuracy, the possible sources of error, the defects in the processes, the conditions requiring a variation of the procedure, etc.

In one case thirteen, and in others nearly as many, separate notes of this kind are given. It takes, for example, fourteen pages of the book to explain how to deal with the elements of the iron group. While these notes are an excellent feature for students who have become familiar with the usual procedure, it is to be feared that the complexity of conditions they discuss, may confuse the beginner. The description of the procedure is, in most cases, incomplete without the notes, as the appearances

to be expected from the substance tested for are not given. One is obliged to hunt among the notes for the color or appearance of precipitates, etc.

But one test for each metal is given, as a rule, and nowhere are confirmatory tests given. The author plunges the student at once into the separations of the groups, omitting the usual preliminary tests for individual metals, except as they come in the separation. While there is some truth in his statement, that too much of this work is a waste of time, several confirmatory tests for each substance should be found in a complete course in qualitative analysis. Only the more difficult reactions are written out for the student.

There is neither index nor table of contents, which seriously impairs its usefulness for ready reference. While we have pointed out what seem to us its defects, especially for beginners, we must regard its main features as excellent, because of the full explanatory notes. Its chief claim to novelty is in this one feature.

E. H. BARTLEY.

VOL. XVI. AUGUST, 1894. No. 8.

THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.

THE ACCURACY OF THE COMMERCIAL ASSAY FOR SILVER.[1]

BY FREDERIC P. DEWEY.

IT is generally considered that the fire assay for silver is remarkably accurate when properly carried out. Ricketts says, page 79, "The assay for gold and silver, if conducted carefully, is one of great accuracy. Duplicates of silver should agree to within one-half ounce Troy per ton" (xxx).

In general, and particularly when only small amounts of silver are present, the prevalent idea is correct, but, as shown by the above extract from Ricketts, in considering the accuracy of silver assays, too much stress is laid upon the agreement between duplicates, and I hope to show that, while the actual accuracy of the ordinary fire assay is, in many cases, very great, yet for commercial purposes still greater accuracy is required.

The main conditions which lead to accuracy are the possibility of using large quantities of material and the accuracy attainable in weighing the button, and these apply more particularly when only small amounts of silver are present. When, however, large quantities of silver are present we cannot carry on the process so successfully with so large a quantity of material, and, if we could, we might get a button too large to weigh on a button balance, and thus sacrifice some delicacy of weighing.

It has long been known that there are three sources of loss in assaying; first, from silver going into the slag; second, by silver absorbed by the cupel; third, from volatilization of silver. In dealing with rich materials corrections have been applied, and in the case of bullion it has been sought to correct for all losses by

[1] Read before the Washington Section, April 12, 1894.

running a check assay as near as possible like the test. When, however, we come to consider large quantities of ore, even though they carry only a moderate number of ounces of silver per ton, it is found that greater accuracy of assay for silver is necessary even for this class of material.

This is most clearly shown by a "clean-up" run by the Russell process for lixiviating silver ores. Fifty tons of ore, carrying by the ordinary assay 2,178 ounces of silver, or 43.43 ounces per ton, were treated by the Russell process, and 2,149 ounces of silver recovered, or 99.6 per cent. of the silver shown by the ore. In addition to this the tailings showed 272.25 ounces, or 12.5 per cent. Making a total of 111.5 per cent.

After a thorough investigation of this anomalous result the samples were re-assayed, but the slags and cupels were saved and also assayed, and the results added to the main assay. By this proceeding the ore showed 3.53 ounces more per ton, and the per cent. of silver saved was reduced to 91.5 per cent. Adding to this the 12.5 per cent. remaining in the tailings we have 104 per cent. The increase of silver found in the slag and cupel amounted to 8.1 per cent. of the silver in the ore, and the excess of 4 per cent. on the total may perhaps be assumed as about the volatilization loss in this case.

Attention having been called to the importance of this well-known, but hitherto unappreciated inaccuracy in silver assaying, the Russell Process Company has collected many statistics upon the subject, and I am indebted to a forthcoming pamphlet upon the subject of "plus clean-ups" for much information. I am also indebted to Mr. H. E. Wood, assayer, of Denver, Col., and to the Dewey-Walter Refining Company for many figures used in this paper.

In general, the percentage of the inaccuracy of the ordinary commercial assay varies inversely with the value of the material assayed when figured upon that value.

In order to see this most clearly it is necessary to compare results on the same class of material, and, preferably, made by the same assayer under practically constant conditions. Sometimes when a series of individual results differs irregularly, if the results are grouped considerable regularity may appear. For

instance, on looking at a series of miscellaneous results on ores running from fifteen to forty ounces per ton no regularity may appear, but if the results are grouped in periods differing by five ounces per ton they may become very regular in the variation. While different assayers working on the same material may show some regularity, they may also vary greatly.

For instance, a group of results on tailings arranged according to the increase in value by commercial assay shows as follows:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1- 3	1.8	0.5	2.3	21.8
"	"	2.8	0.4	3.2	12.5
"	3- 5	3.0	0.6	3.6	16.7
"	"	3.9	1.0	4.9	20.0
"	"	4.0	0.5	4.5	11.4
"	5- 7	5.5	0.6	6.1	10.0
"	"	6.0	1.3	7.3	17.8
"	"	6.2	1.2	7.4	16.1
"	7- 9	7.5	1.4	8.9	15.7
"	"	8.3	0.9	9.2	10.1
"	9-11	9.6	1.6	11.2	14.3
"	"	9.7	1.6	11.3	14.2
"	"	9.8	1.3	11.1	10.0
"	11-13	12.2	1.8	14.0	13.0
"	15-20	17.5	1.6	19.0	16.9
"	"	18.5	1.8	20.3	8.9

When, however, we take out of this table the results by a single assayer, we have:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1- 3	1.8	0.5	2.3	21.8
"	3- 5	3.9	1.0	4.9	20.
"	5- 7	6.0	1.3	7.3	17.8
"	7- 9	7.5	1.4	8.9	15.7
"	9-11	9.6	1.6	11.2	14.3
"	11-13	12.2	1.8	14.0	13.
"	13-20	18.5	1.8	20.3	8.9

When we group results by five ounce periods we have:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Tailings.....	1– 5	2.8	0.7	3.5	18.
"	5–10	7.8	1.4	9.2	15.2
"	10–15	12.2	1.8	14.0	13.
"	15–20	18.0	1.7	19.7	8.6

It has been found that the character of the ore influences the results. In three kinds of ores, base, containing seventy-five per cent. sulphurets, partially oxidized, and completely oxidized, carrying from 16.5 to 34.6 ounces of silver per ton, the percentages of silver found in the slag and cupel were as follows:

Base.	Intermediate.	Oxidized.
5.7	8.2	9.8
6.8	7.8	11.3

the results on the top line being obtained by scorification and those on the bottom line by crucible assay, of the same ore in each case.

It follows then, that when ores consisting of mixtures of altered and unaltered material are considered, the proportion between these two should be known and allowed for when comparing results on similar grades of ore, if one would discover the regularity in the variation of the results.

Again, whether the ore is raw or roasted, or has been washed, influences the result, roasted ore being generally more inaccurate than raw.

A heterogeneous table of results on ores running from ten to fifty ounces per ton is as follows:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Ore	10–15	12.5	1.3	13.8	6.4
"	15–20	17.6	1.8	19.4	9.0
"	20–25	22.4	1.9	24.3	7.8
"	"	23.1	2.0	25.1	8.0
"	"	23.8	4.8	28.6	13.0
"	"	23.9	4.5	28.4	15.8
"	"	24.1	5.9	29.7	18.8
"	"	24.3	3.3	27.6	12.0
"	25–30	26.6	2.5	29.1	8.6
"	"	27.	4.0	31.0	13.0

Material	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Ore	25–30	27.2	2.9	30.1	9.7
"	"	28.	4.6	32.6	14.1
"	"	28.4	3.	31.4	9.0
"	"	28.9	1.6	30.5	5.0
"	"	29.7	2.8	32.5	8.6
"	30–35	30.4	3.6	34.0	10.6
"	"	30.6	2.0	32.6	6.1
"	"	30.7	3.9	34.6	11.3
"	"	31.6	3.4	35.0	10.0
"	"	31.8	2.3	34.1	7.0
"	"	31.9	3.9	35.8	10.9
"	"	32.3	3.7	36.0	10.0
"	"	33.	4.1	37.1	10.8
"	"	33.1	2.8	35.9	7.8
"	"	33.6	3.2	36.8	8.7
"	35–40	36.7	3.1	39.8	7.8
"	"	36.9	3.3	40.2	8.2
"	"	37.4	4.3	41.7	10.0
"	"	37.65	2.25	39.9	5.6
"	"	38.2	2.8	41.0	6.8
"	40–45	42.1	3.	45.1	6.7
"	"	42.3	2.3	44.6	5.2
"	"	42.4	2.4	44.8	5.4
"	"	44.7	4.3	49.	8.8
"	45–50	45.5	2.4	47.9	5.0

The variation shown by the above table is very diverse, but the following grouping by five ounce periods, and according to the character of the ore, shows the inverse variation beautifully:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage in slag and cupel.
Roasted ore ..	20–25	23.5	3.2	26.7	12.
" " ..	25–30	27.3	3.5	30.8	11.4
" " ..	30–35	31.6	2.8	34.4	8.1
" " ..	35–40	36.8	3.2	40.0	8.
" " ..	40–45	42.3	2.7	45.0	6.
Raw ore.....	20–25	24.2	4.6	28.8	16.
" "	25–30	27.7	3.5	31.2	11.2
" "	30–35	31.8	3.8	35.6	10.7
" "	35–40	37.5	3.3	40.8	8.1
" "	40–45	43.5	3.3	46.8	7.1
" "	45–50	45.5	2.4	47.9	5.

While the amount of silver recovered from the slag and cupel in the case of ordinary ores is small, when stated per ton of ore, yet when a year's operations, involving ten, twenty, thirty, or more thousands of tons, are considered the difference between an ordinary and a corrected assay amounts to quite a respectable sum, and becomes well worthy of consideration in these times of low prices for silver.

When we consider rich materials, such as high-grade ore and the products of the Russell process, for instance, the slag and cupel loss on a single ton becomes considerable, and with very rich products, such as lixiviation sulphides, particularly when they carry a large percentage of copper, as in the regular Russell sulphides, this loss may amount to several hundred ounces per ton. It has been customary to use the slag and cupel assay on rich products and it was employed on the "clean-up" referred to.

I am indebted to Mr. H. E. Wood, assayer, No. 1,744 Arapahoe St., Denver, Col., for a series of results on sulphides, varying from poor to rich.

The following details give the results on assaying sulphides—scorification method. 1–20 A. T. of sulphides used, and scorification slag and cupel from original assay then rescorified and cupelled with result shown. Classified according to the grade the losses were as follows:

Under	500	Average of	1 Lot.....	4.170 per cent.
500 to	1,000	" "	6 Lots.....	2.910 " "
1,000 "	1,500	" "	14 "	2.996 " "
1,500 "	2,000	" "	9 "	2.540 " "
2,000 "	2,500	" "	12 "	2.109 " "
2,500 "	3,000	" "	21 "	1.867 " "
3,000 "	3,500	" "	19 "	1.860 " "
3,500 "	4,000	" "	19 "	1.821 " "
4,000 "	4,500	" "	10 "	1.695 " "
4,500 "	5,000	" "	7 "	1.700 " "
5,000 "	5,500	" "	4 "	1.845 " "
5,500 "	6,000	" "	4 "	1.895 " "
6,000 "	6,500	" "	1 Lot.....	1.630 " "
6,500 "	7,000	" "	4 Lots.....	1.777 " "
7,000 "	7,500	" "	2 "	1.640 " "
7,500 "	8,000	" "	1 Lot.....	1.420 " "
8,000 "	8,500	" "	3 Lots.....	1.537 " "
9,000 "	9,500	" "	3 "	1.460 " "

10,500 to 11,000	Average of	1	Lot	1.570	per cent.
11,500 " 12,000	"	1	"	1.340	" "
12,000 " 12,500	"	1	"	1.270	" "
17,000 " 17,500	"	1	"	1.260	" "

The average slag and cupel absorption on the 144 lots was 2.03 per cent. of the total contents.

The following table shows the results obtained on eleven lots of regular Russell sulphides when assayed by the following method:

"Weigh out one-twentieth ($\frac{1}{20}$) of an assay ton of sulphides, fifty-five grams of granulated test-lead, and two (2) to three (3) grams of fused borax. One-half of the lead is put in the bottom of the scorifier and hollowed out; the sulphides are put into the hollow and the rest of the lead poured over them; the borax is then placed on top. The assay is then conducted in the usual way. The slag and cupel shall be ground up and assayed, and the result added to the main assay."

This method is the result of a great deal of work and has been adopted as most suitable for this class of material.

In the table are given, first, the results of plain scorification assay; second, the ounces per ton found in the slag and cupel; third, the percentage in slag and cupel; fourth, the total silver found by adding the slag and cupel silver to the scorification silver by one assayer; fifth, the total silver as found by another assayer upon the same samples, and finally, the difference between the two assayers.

Ounces per ton by commercial assay.	Ounces per ton in slag and cupel.	Per cent. in slag and cupel.	Total ounces per ton.		Differences.	
1st assayer.	1st assayer.	1st assayer.	1st assayer.	2nd assayer.	Plus.	Minus.
8,675.20	144.11	1.622	8,819.31	8,782	37.31	
10,074.25	189.35	1.844	10,263.60	10,119	144.60	
10,783.35	189.	1.720	10,972.35	10,938	34.35	
10,902.30	194.38	1.752	11,096.68	11,220		123.32
11,015.73	191.69	1.710	11,207.42	11,090	117.42	
11,238.40	175.22	1.535	11,413.62	11,548		134.38
11,828.75	176.72	1.471	12,005.47	12,046		40.53
12,566.55	199.21	1.560	12,765.76	12,821		55.24
12,665.85	199.87	1.553	12,865.72	12,841	24.72	
13,001.65	229.84	1.737	13,231.49	13,187	44.49	
13,625.50	226.52	1.635	13,852.02	13,919		66.98

On comparing results on individual lots considerable variation will be found between the two assayers, but on considering the total amount of silver involved the difference becomes quite small. By the first assayer these eleven lots contain 236,418.99 ounces of silver, while by the second they contain 236,483.88 ounces, the difference between the two being only 54.89 ounces. This amount is 0.0232 per cent. of the smallest total of ounces found, and 0.0095 per cent. of the weight of sulphides involved. This shows that when carefully and properly executed the method gives concordant results on averaging a sufficient number of assays.

As showing the difference which may occur by this method of assaying, besides noting the individual difference above, between the two assayers, it may be added that one of these found the following difference on assaying the same sample at different times:

No. 1.....	144	ounces per ton.
" 2.....	90	" " "
" 3.....	112	" " "

Making a difference of 527.36 in the total silver involved.

Also on a lot of sulphides containing 218,324 ounces[1] by one assayer, a second assayer obtained 0.587 per cent. less on the same samples, and in a second comparison between the first assayer and the same smelting works, representing 156,091, the difference was 1.355 per cent.

The following results were obtained in my laboratory by Mr. Charles Earl:

Total silver. Ounces per ton.	Silver in slag and cupel. Ounces per ton.	Percentage in slag and cupel.
9,156.3	244.	2.664
9,590.	257.5	2.685
9,828.2	250.	2.543
10,077.95	198.25	1.967
10,456.	266.	2.544
10,759.	244.5	2.272
10,861.5	282.5	2.6
11,700.2	198.66	1.697
12,087.8	233.3	1.93
13,804.5	250.33	1.813

[1] *Trans. A. I. M. E.*, Pamphlet Edition. Product and Economical Results of the Marsac Refinery for the year 1892, by C. A. Stetefeldt, p. 9.

In using this method Mr. Earl usually starts four assays of each sample. As he has found the charge rather destructive to scorifiers it is not unusual to lose an assay. In two sets of four results the differences between the highest and lowest individual results were 49.6 and 95 ounces per ton. In five sets of three results the differences were 36, 54, 94, 98, and 152.2 ounces per ton. As each one of a set of assays was carried through under practically the same conditions as the others these differences may seem rather high, but the total ounces represented by these seven assays by Mr. Earl was 121,346.53 ounces, while another very expert assayer by this method, working upon the same samples, found 121,446.56 ounces, showing a difference of only 99.93 ounces on the total number of ounces involved The following table shows the individual variations:

Total ounces	per ton.	Differences. Plus.	Minus.
6,769	6,847	..	78
9,400.3	9,430	..	29.7
9,590	9,524	66	...
9,928	9,880	48	...
10,078	10,119	..	41
10,456	10,446	10	...
10,759	10,833	..	74

The following tables summarize a large quantity of determinations and are taken from the pamphlet by the Russell Process Company referred to:

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage slag and cupel.
Lead carbonate...	1– 50	5.2	0.8	6.0	15.4
" " ...	50– 100	64.8	3.2	68	5.1
" " ...	100– 500	447.6	12.4	460	2.6
Base sulphides...	100– 500	394	37	431	8.6
" " ...	500– 1,000	766	41	807	5.1
" " ...	1,000– 1,500	1,227	36	1,263	2.9
" " ...	2,000– 3,000	2,527	88	2,615	3.2
" " ...	3,000– 4,000	3,289	113	3,402	3.2
" " ...	4,000– 5,000	4,962	116	5,078	2.2
Regular sulphides	100– 1,000	493	45	5,538	8.4
" "	1,000– 2,000	1,624	83	1,707	4.9
" "	2,000– 4,000	2,807	60	2,867	2.1
" "	4,000– 6,000	5,291	98	5,389	1.8

Material.	Grade. Ounces per ton.	Value commercial assay. Ounces per ton.	Value in slag and cupel. Ounces per ton.	Corrected value. Ounces per ton.	Percentage slag and cupel.
Regular sulphides	6,000– 8,000	7,362	110	7,472	1.5
" "	8,000–10,000	8,604	128	8,732	1.5
" "	10,000–12,000	10,538	150	10,698	1.5
" "	12,000–14,000	12,842	218	13,060	1.7
" "	14,000–16,000	14,866	180	15,046	1.2
Refinery residues,	14,000–16,000	15,952	159	16,111	1.
	Fine.	Fine.	Fine.	Fine.	
Base bullion	300– 500	400	8	408	2.
Fine "	998–1,000	987	11.5	998.5	1.2

Material assayed.	Grade of value.	Range of inaccuracy.	Average inaccuracy.
Tailings	1– 20	18 – 8.6	13.7
Washed ore.....	15– 35	13 –10.0	10.4
Raw ore.....	20– 50	16 – 5.0	9.7
Roasted ore	20– 45	12 – 6.0	9.1
Lead carbonate	50– 100	5.1– 2.6	3.8
Base sulphides	1,000– 5,500	5.0– 1.8	3.0
Regular sulphides.....	2,000–16,000	2.8– 1.2	1.7
Copper-silver bullion, 300 "fine"		2.0	2.0
Fine bullion, 999.3 "fine"		1.1	1.1

In a number of cases the slag and cupel have been assayed separately, but there does not seem to be any uniformity of results, except that the cupel silver is generally much greater than the slag silver, although in one case they were both the same, 0.8 ounce. In a set of twenty-nine assays, running from tailings at 6.2 ounces per ton to ore at 44.7, the cupel silver varied from 0.8 to 5.4 ounces per ton, and the slag silver from 0.1 to 1.8 ounces per ton; the lowest cupel silver was on 18 ounce ore and the highest on 24.1 ounce ore; the lowest slag silver was on 26 ounce ore, and the highest on 32.4 ounce ore, and both these assays were made by the crucible method. In only two cases was the cupel silver less than 1 ounce per ton, and one of these was on the 6.2 ounce per ton tailings, and in only two cases was the slag silver over 1 ounce per ton.

In the case of the nearly proof silver produced at the Marsac refinery, by the writers process, the straight assay shows 987 fine, corrected for slag and cupel absorption it becomes 998.5 fine, as given in the table, while with a check assay to correct the volatilization loss it becomes 999.3 fine.

When we come to consider the percentage of inaccuracy when figured upon the total material assayed we find that it is somewhat irregular but generally it follows the silver contents of the material, and in the case of rich products, becomes very large. Thus, in 2.3 ounce tailings the silver equals 0.0079 per cent. of the total and a 21.8 per cent. loss on this equals only 0.0017 per cent. of the total. On the other hand, in a 17,500 ounce sulphide the silver equals 60 per cent. of the total, but the comparatively small loss of 1.26 on this equals 0.756 per cent. of the total.

The following table gives a few results upon this point:

Material.	Grade. Ounces.	Silver per cent. of total.	Inaccuracy per cent. of silver.	of total.
Tailings.....	2.3	0.0079	21.8	0.0017
Ore	20.3	0.0696	8.9	0.0062
"	30.5	0.1011	5.	0.0051
"	31	0.1063	13.	0.0138
"	49	0.1680	8.8	0.0148
Base sulphides ...	431	1.477	8.6	0.12602
" " ...	5,078	17.41	2.2	0.38302
Regular sulphides	5,538	18.98	8.4	1.59432
" "	10,698	36.33	1.5	0.54495
" "	15,046	51.58	1.2	0.61896
" "	17,500	60.00	1.26	0.756

The question is sometimes asked if some wet method would not be better than fire assaying, but at present no such method is available.

While the correction for slag and cupel loss is easily made, and ought always to be made when accurate statistics are kept, there is yet the volatilization loss to correct, and some means of doing this is very desirable. While a check assay answers very well for bullion it would hardly be possible to construct check material for the varying characters of ores and products ordinarily met with.

As chemists we should all be interested in attaining the highest accuracy possible in our analytical work, but in this case, aside from the question of accuracy, and also the money value of the silver involved, when many thousand tons of ore are considered, this point has a very important practical application in indicating and bringing out unsuspected losses in mill opera-

tions. For instance, in one case, by ordinary assays of the ore, the mill showed to be extracting 87 per cent. of the silver in the ore, which was considered good work. Corrected assays of the ore showed, however, that the extraction was only 79.3 per cent. This led to an investigation, which showed that there was a volatilization loss of 10.9 per cent. in roasting the ore. This has been cut down to 5 per cent., with the expectation of reducing it still more.

In another case the extraction plus the tailings silver was 102.7 per cent., but corrected assays showed it to be only 87.1 per cent. This was brought up to 97 per cent.

These figures show that the commercial assays of ores are too unreliable if accurate mill statistics are desired.

THE ACHIEVEMENTS AND AIMS OF PHYSICAL CHEMISTRY.[1]

By J. E. Trevor.

Received June 7, 1894.

CHEMICAL changes, in common with all other natural processes, are in their ultimate nature transformations of energy. The study of chemical processes is therefore a study of the energy phenomena which they involve. Chemical reactions may absorb or take up heat, changes of density may occur whereby work is done, electrical energy and radiant energy may be produced. But the mutual relations of heat, work, electricity, and the like, involving the characteristic factors, temperature, pressure, tension, force, potential, etc., form the subject-matter of the science of Physics, and hence it is that the study of chemical processes as such has come to be known as the *Physical Chemistry*. The object of this branch of science is to discover the simple relations connecting the various types of chemical phenomena, and to make of these relations a coherent whole.

The Physical Chemistry is a new science. Up to eight years ago nothing serious had been attempted in the way of generalization. Very important discoveries had been made before that time it is true, yet they where of a wholly disconnected character and their bearing upon a general theory of chemical processes

[1] Read before the Midwinter Fair Congress of Chemists at San Francisco, June 7, 1894.

was not seen. Prominent among these achievements of a generation whose efforts have now become history stand the experimental work of Thomsen and Berthelot in thermo-chemistry, the investigations of Kopp in stoichiometry, the dissociation theory of Horstmann and of Gibbs, the brilliant researches of Helmholtz in electro-chemistry, and that flash of insight which led to the discovery of the law of mass action. Nor is the present generation proving itself unworthy of this inheritance of scientific achievement; the chemical equilibrium, the electro-chemistry, and the thermodynamical generalizations of to-day are supplying a fit sequel to this story of the past.

In 1886 appeared van't Hoff's first paper upon the theory of solutions. It was immediately followed by that extended series of monographs, written by such men as Ostwald, Nernst, Arrhenius, Planck, Riecke, and many others, which has made the thermodynamical theory of solutions one of the most remarkable conquests of the science of chemistry. Van't Hoff's discovery that the inner energy of a dissolved substance when dilute is independent of the volume of its solution led at once to the discovery of simple relations between the physical properties of solutions and their molecular concentrations, *i. e.*, to a series of novel methods for the determination of molecular weights; it brought about an unforeseen extension of the law of mass action to the solution-equilibria of both homogeneous and heterogeneous systems; it led to a strict formulation of the influence of temperature upon chemical equilibrium and the velocities of reactions, to a mathematical theory of hydrodiffusion, to a comprehensive theory of concentration currents and of the voltaic cell, and to an unexpected culmination of Ostwald's exhaustive investigations upon the chemical affinities of aqueous acids and bases. This breathless succession of advances constitutes one of the most interesting and exciting chapters of the history of chemical theory.

It is being succeeded at the present time by work of a more general and wide-reaching character. The great generalizations of thermodynamics are hastening the day when chemistry shall become a deductive science. Planck, of Berlin, has recently directed especial attention to the following course of reasoning.

There are certain processes, such as the conduction of heat from a hot to a cold body, or the diffusion of a dissolved substance from a high concentration to a lower one, which are irreversible—they take place only in one direction. This fact may be shown to require the conclusion that the general trend of natural processes is in an assignable direction; the general state of things tends all one way. If this were not so it would be possible to reverse history, to make trees grow down into seeds, and to awaken fossils to quivering, pulsating life.

The strict formulation which represents this general tendency furnishes, therefore, a means of determining definitely the direction which any given natural process, chemical or otherwise, must pursue; and it leads in consequence to an exact relation between the energy factors upon which the final state of the material system concerned is made to depend, a relation which combines in one expression every law of chemical equilibrium. From it can be derived in order all the laws of isothermal chemical equilibrium in homogeneous and in heterogeneous systems, and those which represent the effect of changes of temperature and of pressure in displacing such equilibria; it yields further the laws relating to the many physico-chemical properties of solutions which depend upon the vapor pressures; and it furnishes, finally, the almost numberless theorems of electro-chemistry. Thus it is seen that from the assumption of a simple fact of experience, the irreversibility of heat conduction, a mathematical theory of chemical changes is obtained which organizes into a coherent and logically connected whole all the exact relations of chemical science. The deductive value of this theory is enormous, in that it clearly points out the limits of our knowledge in every direction. And for the reason that the system is uniform and falls into a logical order it becomes of the greatest service in aiding the conception of chemical theory as a whole and in fixing in the mind the relations between its parts.

Another form of the same fundamental idea has been employed by the eminent French mathematical physicist, Duhem, in developing a systematic treatment of the theory of chemistry. From the properties of his *thermodynamical potential* (taken from the thermodynamical studies of Willard Gibbs) he has evolved

an orderly discussion of the theory of dissociation, the continuity of the liquid and gaseous states, and the general theory of the chemical and physical equilibria of fluid mixtures, all of which is characterized throughout by strict uniformity of method and an unusual elegance of mathematical style.

These two methods of research are essentially identical, for they are based upon the same principle, and they both refer the solution of every problem to the properties of a single function of quantities which fix the state of the system concerned. In this respect they mark a distinct advance in the study of the science of chemistry.

The eminent fruitfulness of these thermodynamical methods has led to a fuller appreciation of the bearing and significance of the great energy generalization which they involve, and upon which, indeed, the entire framework of modern physical science really rests. If chemistry be in its ultimate nature, an energy science, chemists obviously must study those energy transformations which constitute its phenomena. In a chemical change different energies come into play, and the change continues until they hold one another exactly in balance. This balance determines, therefore, what the final state of the system in question shall be. Two energy forms are in equilibrium when a possible variation of one is exactly compensated by the corresponding variation of the other. All that is necessary then to determine the final state which any given material system must assume is to represent mathematically the possible variations of its opposed energies and to set these variations equal. This procedure is identical with that which is employed in Statics to investigate the equilibria of mechanical systems. When applied systematically to the different types of chemical action it yields a rational classification of chemical processes, and, in a logical sequence, all of the known elements of the modern physical chemistry. This reconstruction of theoretical chemistry upon the basis of the Energy Theory is one of the most brilliant of Ostwald's many splendid contributions to science.

It is important to observe that the great advances of recent years in the theory of chemical action have not been made with the aid of the kinetic-molecular hypothesis. The assumption of

atoms and molecules has been a constant hindrance to the progress of rational chemical theory. The "Kinetic Theory of Gases" has been able to account for the behavior of gases only in an imperfect manner, and it has not been able to account at all for the laws of chemical equilibrium and the properties of solutions. The fact that gases react in simple volume relations justifies the selection of a definite volume as the chemical unit, the relative weight of this volume becoming then the so-called molecular weight, but it justifies in no wise the conclusion that gases are composed of discrete particles. This unwarranted assumption was made because of a desire to "explain" from the behavior of a purely mechanical system the observed characteristics of gases. Yet the behavior of the model is, after all, only approximately that of the gas. And, moreover, it is not the province of science to "explain" anything, certainly not to explain phenomena by reference to irrealizable mechanical constructions. It is becoming more and more clearly seen, day by day, that the business of science is to *describe* phenomena in a simple manner, to seek actual relations between measurable quantities, to deal only with things which can be handled and observed. Hypotheses must be employed, if at all, only provisionally and as analogies.

There is no desire to deny that the molecular hypothesis has been fruitful of results; any hypothesis may lead to work whereby knowledge is gained. Yet this one has nearly outlived its usefulness, and it will be employed less and less in the future by those chemists who refuse to believe upon insufficient evidence. As an accepted hypothesis its days are numbered. In the place of the Molecule appears the Molecular Weight, a sharply defined quantity whose conception does not transcend experience.

The average student of chemistry is trained to confuse the real with the hypothetical. He believes molecular formulas and molecules to involve each other, whereas, the former represent facts while the latter are creations of fancy. The molecular formulas of our chemical equations possess a very real and important signification, and this is no less true of the structural formulas which form at the present time so important a feature of the technical apparatus of organic chemistry. These structural formulas

are valuable mnemonic expressions for the individual chemical character of the substances in question, and when employed for what they represent their value is not to be underestimated. Yet one must not for a moment suppose that they supply a picture of the mechanical structure of small particles of the substances; this idea is a purely hypothetical one, and at the best represents nothing more than the original facts. The symbols, properly used, represent the facts and not the hypothesis.

The general methods which give to the best modern thought its distinctive character appeal to experience alone. Things other than observable fact do not fall within their province, such things are not objects of human knowledge. It should not need emphasis that this is the only natural and reasonable basis for a science of the facts of nature. And it cannot be denied that our first real insight into the nature of chemical processes has been gained by the application of these straightforward methods.

The age of mechanical hypotheses is of the past. The desire to replace known laws by unproven or unprovable assumptions is passing away. And it can now be clearly recognized that the view which seeks to place mechanics at the base of all departments of physical science is, in its thoughtless exclusion of energies other than mechanical, a prejudice. Now, the thermodynamical systems and the energy doctrine involve only accessible facts. They are built upon no assumption other than the irreversibility of some spontaneous process, or the observed conservation of the energy of an isolated system. Their aim is to increase knowledge, and not representations of knowledge, to seek out the facts of nature and the wonderful and simple relations subsisting among these facts. And in this there are notable instances of what is fittingly termed *Physical Theory*. The distinction between theory and hypothesis can now be sharply drawn, the Hypothesis is a mechanical construction substituted by the imagination for things as they actually are, the Theory is an organized system of logical consequences drawn from the established facts of experience. Mechanical Hypotheses have dimmed the glory of the history of chemistry, Physical Theory endows chemistry with the attributes of an exact science.

The subject of electro-chemistry has become, in recent years, a

prominent feature of the physical chemistry. The energy liberated in chemical changes may appear as electrical energy; or electrical energy may, during a chemical process, be transformed into the inner energy of the products of the reaction. Our knowledge of these things has had a contentious and a profoundly interesting history. The strugglings and gropings of a hundred years lie between this time and that in which the first observations of electro-chemical action were made by Galvani and Volta. The intervening years have been largely occupied by a study of the phenomena of electrolysis pure and simple. The insight thereby gained into the nature of this process has led to a clear conception of what takes place in the various types of voltaic cell, and has, in consequence, rendered accessible to immediate calculation all the essential details of the transformation between the free energy of the chemical action in a cell and the electrical energy which is produced. This comprehensive theory of electro-chemistry is one of the greatest results which has followed the introduction of the energy theory into chemistry, it is the fitting close of a century of effort.

And now that such a result has been reached it is a matter for congratulation that the event is to be marked by a great literary monument. This is Ostwald's work on electro-chemistry, at the present moment passing through the press, a book which is to give a full and clear account of the entire development of the subject from its beginnings.

The influence which has been exerted upon physical chemistry by its literature is of the most interesting character. Widespread interest in physical chemistry as an independent subject dates, probably, from the publication of Ostwald's *Lehrbuch der allgemeinen Chemie*, in 1887. The interest thus aroused was immediately intensified by the appearance of van't Hoff's thermodynamical theory of dilute solutions, and the remarkable series of theoretical and experimental discoveries which followed in its train. This period marks, undoubtedly, the beginning of physical chemistry as a connected and organized science. Its development since then, due to no small extent to the efforts of Ostwald and van't Hoff and their pupils, has found a fit channel for expression in the pages of the *Journal of Physical Chemistry*

(*Zeitschrift für physikalische Chemie*), whose first number appeared also in 1887. A systematic account of the present status of the science is now being supplied by a new edition of Ostwald's *Lehrbuch*, which has in the meantime grown to be a monumental work in three volumes, two of which are already in print. And it is well to add that the general desire for a text-book of less exhaustive nature has been well met by the briefer "*Outlines*" by the same author, and the "*Theoretical Chemistry*" of Nernst. Due reference has been already made to Ostwald's magnificent publication upon electro-chemistry.

The great demand now to be made upon the future is for a book upon the *General Theory of Energy;* a work in which the relations of natural phenomena to one another may be brought into a clear light, a work in which we may finally see effaced the artificial distinctions between the subjects of Chemistry, Mechanics, Thermodynamics, Electricity, etc., which, as we have them now, are partly historical, partly physiological, partly conventional, and wholly unsatisfactory.

The science of Physical Chemistry is, at the present moment, in a stage of the most active development. Every month brings to the light some startling experimental discovery, or some broader generalization. The general methods now in use have already begun to furnish a complete thermodynamical theory of solutions for all concentrations, a thorough grasp of the conditions of chemical equilibrium in complex heterogeneous systems, a really adequate comprehension of the phenomena of galvanic polarization, and an exact definition of chemical affinity. These are the things of to-day, what the morrow may bring forth is for no man to say. Yet it is certain that the chemistry of the future will deal with fact and not with fancy, and that its immediate aim will be the establishment of exact relations between those quantities upon which the state of every material system ultimately depends. For it is in this way, and in this way only, that a real insight into the nature of chemical processes will finally be attained.

CORNELL UNIVERSITY,
May, 1894.

PROTEIDS OF THE WHEAT KERNEL.[1]

By Thomas B. Osborne and Clark L. Voorhees.

THE importance of wheat as a breadstuff, and the fact that its superiority over all other cereals for bread-making mainly depends on the properties of the proteids composing the gluten which wheat dough yields when cautiously washed with water, justify giving here in some detail an account of the present state of knowledge regarding the proteids of wheat.

The wheat used in our work was of two kinds. One of these, Scotch Fife, a hard spring wheat, raised in Minnesota, was obtained through the kindness of Dr. D. N. Harper, late chemist of the Minnesota Experiment Station. It was carefully selected, free from all other varieties, and was milled under the supervision of Dr. Harper, who supplied us with samples of the various mill products, together with some of the unground wheat. Two grades of flour were used; namely, "patent flour," made from the finest and purest middlings, and "straight flour," from the coarser and less pure middlings. The "shorts," chiefly composed of the outer coating of the seeds together with adhering portions of the endosperm, was also examined. Samples of whole wheat flour were prepared as required from the wheat by grinding small quantities in the laboratory mill. The other wheat used was a variety of winter wheat known as "Fultz." This was procured from Mr. F. S. Platt, seedsman, of New Haven, and was carefully selected and freshly harvested.

When wheat flour or meal is made into a stiff dough with water and then carefully kneaded or squeezed in a gentle stream of water, the starch which makes up 60–68 per cent. of the flour or meal is gradually washed away for the most part, and there remains a tough elastic sticky mass.

The first published description of this body was made by Beccari in 1745 who gave it the name it still bears; *viz.*, *Gluten*.

In 1805 Einhof observed that hot alcohol extracts from wheat flour a substance resembling gluten. In 1820 Taddei showed

[1] First printed in the Report for 1893 of the Connecticut Agricultural Experiment Station, New Haven; communicated by the author.

that gluten contains two substances, one soluble the other insoluble in boiling alcohol.

Since 1820 many chemists have undertaken to investigate gluten but their conclusions as regard the number, properties and composition of the proteids it contains, are extremely discordant. Einhof, Boussingault, Bouchardat, Denis, Weyl and Bischoff and Martin have considered gluten to consist essentially of a single proteid. Berzelius, DeSaussure, Liebig, Dumas, and Cahours, and Von Bibra, believed it to contain three, while Ritthausen and Bechamp regard it as composed of four proteids.

We have separated from the wheat kernel five distinct proteids; *viz.*, Gliadin, Glutenin, a Globulin, an Albumin and a Proteose. A proteose-like body, apparently distinct, was also obtained, but in too small quantity for satisfactory examination.

The mode of isolating these substances in a state of comparative purity and establishing their individuality, is fully stated in a former paper,[1] to which reference must be made for details.

Of these proteids only the first two properly belong to gluten.

I. *Gliadin* is the proteid which is readily dissolved from wheat flour and from gluten by hot dilute alcohol. It also exists in the rye-kernel.

This substance when dehydrated by absolute alcohol and thoroughly dried over sulphuric acid, forms a snow-white, friable mass which is easily reduced to a powder. If dried after being moistened with dilute alcohol or water it resembles, in appearance, pure gelatin. Dried thus, in thin sheets it is perfectly clear and transparent but is rather more brittle than gelatin. When treated in the cold with distilled water it becomes sticky and slightly dissolves. If the water is warmed, more dissolves and on boiling, much goes into solution. Solutions in warm water on cooling, deposit a part of the substance. The solution in pure water is instantly precipitated by adding a very minute amount of sodium chloride.

In absolute alcohol gliadin is entirely insoluble, but dissolves on adding water, the solubility increasing with the addition of water up to a certain point, and then diminishing. The exact degree of solubility for various strengths of alcohol has not been

[1] *Am. Chem. J.*, 15, 392.

determined, but mixtures of about seventy per cent. of alcohol and thirty per cent. of water dissolve the proteid in almost indefinite amount. From solutions in strong alcohol as well as from those in very weak alcohol the proteid is precipitated by adding a few drops of solution of sodium chloride, the completeness of precipitation depending on the strength of the alcohol and the amount of salt added. The more the alcohol varies in strength from seventy to eighty per cent. the more completely is the substance precipitated.

In extremely dilute acids and alkalies this proteid is readily soluble, and is precipitated from such solutions on neutralization apparently unchanged either in properties or composition.

Gliadin gives with Millon's reagent, with nitric acid and with the biuret-test, the usual proteid reactions. Dissolved in concentrated hydrochloric acid, a beautiful violet color develops slowly. With warm fifty per cent. sulphuric acid a similar color appears which is greatly increased in intensity on boiling.

On boiling its aqueous solutions, gliadin coagulates and becomes insoluble both in alcohol and in 0.2 per cent. potash solution, but is not thus converted into glutenin, the latter being soluble in weak alkali.

Gliadin was so called by Taddei because of its resemblance to glue. It has also been called plant-gelatin by Liebig, and glutin by Dumas. The plant-casein of Dumas, the mucin of De Saussure and Berzelius, the gluten-fibrin and wheat-mucedin of Ritthausen, are impure gliadin.

Gliadin is entirely distinct in composition from the alcohol soluble proteids of barley, maize, and oats. We found in Fife wheat, 4.33, and in Fultz, 4.25 per cent. of gliadin.

Our analyses of these gluten proteids are as follows:

	Gliadin of wheat, average of twenty-five analyses.	Gliadin of rye, average of thirteen analyses.	Glutenin of wheat, average of eight analyses.
Carbon	52.72	52.75	52.34
Hydrogen	6.86	6.84	6.83
Nitrogen	17.66	17.72	17.49
Sulphur	1.14	1.21	1.08
Oxygen	21.62	21.48	22.26
	100.00	100.00	100.00

II. *Glutenin.* Characteristic reactions of a proteid body which

can be dissolved only in dilute acids or alkalies are necessarily very few in number. Our preparations of glutenin after drying over sulphuric acid, were found to yield to distilled water, especially when warm, a little proteid substance. Diluted alcohol also dissolved a minute amount of proteid matter in the cold, and when heated to boiling, a much greater quantity. It is questionable whether the substance dissolved by water and by alcohol was not a trace of gliadin which had failed to be completely extracted in the process of preparing the glutenin. The fact that the solution in hot alcohol began to precipitate at once on cooling, and that especial care had been taken in every case to remove the gliadin, makes it probable that glutenin is slightly soluble in water and in alcohol, especially if these are warmed.

In very dilute alkalies, as 0.1 per cent. potash solution, and in very dilute acids, as 0.2 per cent. hydrochloric acid, glutenin, after dehydration with absolute alcohol and drying over sulphuric acid, is slowly soluble, with the exception of a greater or less amount of coagulated residue, depending on the circumstances of its preparation. When freshly precipitated, and in the hydrated condition, it is extremely soluble in the slightest excess of caustic alkali, and in a somewhat greater but still very slight excess of acid. In this condition it is also soluble in the slightest excess of sodium carbonate solution or ammonia. After drying over sulphuric acid it dissolves partly in 0.5 per cent. sodium carbonate solution.

Dissolved in concentrated hydrochloric acid it gives a solution slightly yellowish at first, but becoming a deep violet color on standing. In sulphuric acid diluted with an equal volume of water the solution is brownish in color after boiling, and remains clear when diluted. The undiluted solution, on standing, retains its brown color.

A comparison of the analyses of glutenin with those of gliadin shows a very close agreement of the two in composition. As it is well known that many proteids readily lose their solubility without change of composition detectable by analysis, it might seem proper to consider this body as an altered and insoluble gliadin.

There is, however, no evidence that gliadin is actually trans-

formed into glutenin, and since very recent investigation shows that rye-grain contains gliadin, but probably not glutenin, it would appear that the two are to be regarded as distinct.

This proteid, in an impure state, has been termed by various investigators zymom, plant-fibrin, gluten-casein, and gluten-fibrin. As all these names are associated with confused and erroneous notions as to its composition, origin, and properties, they are all properly discarded in favor of the new designation, glutenin.

In Fife wheat we found 3.96, and in Fultz, 3.91 per cent. of glutenin. The other proteids in the wheat kernel are—

III. *Edestin*,[1] a *globulin* belonging to the vegetable vitellins, soluble in saline solutions, precipitated therefrom by dilution, and also by saturation with magnesium sulphate, or ammonium sulphate, but not by saturation with sodium chloride. Partly precipitated by boiling, but not coagulated at temperatures below 100°. The wheat kernel contains between 0.6 and 0.7 per cent. of this globulin. When dried at 110° its composition was found to be as below stated.

IV. *Leucosin*,[2] an *albumin*, coagulating at 52°, unlike animal albumin in being precipitated on saturating its solutions with sodium chloride or magnesium sulphate. It is not precipitated on completely removing salts by dialysis in *distilled* water. It was found to form between 0.3 and 0.4 per cent. of the wheat kernel, and to have the following composition when separated from solution in the coagulated form by heating to 60° C.:

	Edestin.	Leucosin, coagulated.	Coagulum from proteose.
Carbon	51.03	53.02	51.86
Hydrogen	6.85	6.84	6.82
Nitrogen	18.39	16.80	17.32
Sulphur	0.69	1.28	24.00
Oxygen	23.04	22.06	
	100.00	100.00	100.00

V. A *proteose*, precipitated (after removing the globulin by dialysis, and the albumin by coagulation) by saturating the solution with sodium chloride, or by adding twenty per cent. of sodium chloride and acidifying with acetic acid. This body was

[1] Ἐδεστὸς edible.

[2] Λευκὸς white.

not analyzed in its unaltered form. On concentrating its solutions by boiling, a *coagulum* was gradually developed which formed about 0.3 per cent. of the wheat kernel and had the composition given above.

VI. The solution filtered from the substance just described (V.) still contained a *proteose-like body* which was not obtainable in a pure state. Its amount could only be roughly estimated by precipitating the concentrated filtrate from the preceding substance with alcohol, and multiplying the nitrogen contained in the precipitate by 6.25. The amount of this proteose was from 0.2 to 0.4 per cent. of the seed. Both this proteose and the above coagulum are unquestionably derivatives of some other proteid in the seed, presumably the proteose first mentioned.

The Formation of Gluten.—Wheat, as far as is known, is the only plant whose seeds contain proteid matter separable in a coherent form from the other constituents by washing with water. When ground fine and mixed with a suitable quantity of water it yields a dough from which a light, porous bread can be made. The importance of this fact in bread-making is so great that considerable attention has been paid to gluten by the chemists who have studied wheat proteids.

The investigations of Günsberg and of Martin, as well as our own, disprove the existence of gluten-fibrin and mucedin, which are currently stated to exist in gluten, and demonstrate that, as Taddei maintained, gluten consists of two proteids only.

Weyl and Bischoff have asserted[1] that the proteid matter of the wheat kernel is *chiefly a globulin substance*, and that in contact with water it undergoes a change, presumably through the influence of a ferment, by which gluten is first produced.

The statements of these investigators are not sustained by any sufficient evidence. They say: "On investigating the proteids of wheat meal, one of us found principally a globulin substance, which he designated, in consequence of its similarity to myosin of the muscle, *vegetable myosin*. This vegetable myosin must be the mother-substance of the gluten, since in the wheat meal, together with it, other proteids, if at all, exist only in very small amount." What the reasons were for concluding that the

[1] *Ber d. chem. Ges.*, 1880, 367.

"myosin" constitutes nearly, if not all, the proteid of the wheat kernel does not appear. In view of our results this statement is certainly erroneous. Direct treatment of the meal with alcohol yields extracts containing gliadin in exactly the same amount as obtained from the gluten made from an equal quantity of flour, and extraction of either flour or gluten with alcohol, after complete exhaustion with sodium chloride solution, also gives the same proportion of gliadin. This substance must therefore exist in the seed, having the same composition and properties as in the gluten, and as it forms one-half of the gluten, it leaves the other half only as possibly derived from a globulin body through the influence of a ferment. If Weyl and Bischoff's view were correct, treatment of the flour with ten per cent. salt solution ought to alter the character and quantity of the gluten obtained, if not altogether to prevent its formation. This is not so, for the usual amount of gluten can readily be obtained from flour made into dough with ten per cent. sodium chloride solution, and then washed with the same until starch is removed.

Weyl and Bischoff next state that, "with the aid of a fifteen per cent. rock salt solution the flour was extracted until no proteid could be detected in the extract; the residue of the meal kneaded with water then gave no gluten. *If the globulin substance be extracted, no formation of gluten takes place.*" We have found that this is true if the flour is stirred up with a large quantity of salt solution, extracted repeatedly with fresh quantities of the same solution until no more proteid is dissolved, and the excess of solution removed by allowing the residue to drain on a filter as completely as possible. If, however, wheat flour is mixed at first with just sufficient salt solution to make a firm dough, this dough may then be washed indefinitely with salt solution, and will yield gluten as well, and as much, as if washed with water alone. This difference is due to the fact that when large quantities of salt solution are applied at once, the flour fails to unite to a coherent mass and cannot afterwards be brought together, as is possible when treated with smaller quantities of solution.

Weyl and Bischoff compare the formation of gluten to that of blood-fibrin from fibrinogen under the influence of a ferment.

They say that the formation of gluten is affected by all the conditions which interfere with the activity of ferments in general. "Large amounts of salt hinder the formation of gluten. Sulphates of magnesium and sodium behave like common salt." These statements are explained by what has been said above.

They tried unsuccessfully to obtain the supposed ferment in the following manner:

"We allowed meal with an equal weight of ninety per cent. alcohol to stand in closed vessels different lengths of time (in one case four months, then several times three to four weeks, frequently only eight to ten days). The vessels were repeatedly shaken and the yellow-colored alcoholic extract was poured off. The residue was freed from alcohol by pressing and evaporating at the ordinary temperature. After it was stirred up with water little or no gluten was obtained. Evidently the globulin substance had been coagulated for the most part by the alcohol." It is clear that if the flour were thus treated, the greater part of the gliadin would be removed. We have found that if flour be extracted with dilute alcohol until the gliadin is removed, and the residue freed from alcohol by exposure to the air, the latter will then yield no gluten when treated with water.

More recently Sidney Martin has advanced a somewhat similar theory of the formation of gluten from the proteids contained in the seed. He states[1] that alcohol extracts from gluten but one proteid substance; that this is soluble in hot water, but not in cold, and he therefore calls it an *insoluble phytalbumose*.

The residue of the gluten not dissolved by alcohol is uncoagulated proteid, if the alcohol has not been allowed to act too long. This substance he names *gluten-fibrin*. Martin further says that gluten dissolves almost completely in 0.2 per cent. hydrochloric acid, or 0.2 per cent. potash solution, leaving a small residue of fat. The solution gives a copious precipitate when neutralized, but the supernatant liquid still contains a quantity of proteid, which is the dissolved insoluble albumose. The whole of the gluten-fibrin is reprecipitated by neutralization, that is, it is wholly converted into an "albuminate."

Martin then asks: "Does flour contain gluten-fibrin? Does it

[1] *British Medical Journal*, 2, 104, *1886*.

contain insoluble phytalbumose?" The first question he says can not be answered directly. "The second is answered by extracting flour with seventy-six to eighty per cent. alcohol. This ought to contain the insoluble albumose if it were present as such in the flour, *but it does not contain it;* it extracts only fat." This statement is contrary to our experience, for we have never failed, in many experiments, thus to extract this substance (gliadin) from the flour, and that too in the same amount and of the same properties and composition as from the gluten.

Martin concludes that insoluble albumose is not present as such in the flour. He then says: "Before proceeding to mention its precursor, it will be well to state that ten per cent. sodium chloride solution extracts from flour a large quantity of globulin and of albumose. This globulin is of the myosin type, coagulating between 55° and 60° C., and precipitated by saturation with sodium chloride and ammonium sulphate. Both the globulin and albumose are present in a much smaller quantity in the watery extract of the flour." From this it is evident that Martin has fallen into the same error as Weyl and Bischoff, mistaking the albumin for a myosin-like globulin, and being greatly misled as to its amount.

Continuing, Martin says: "The direction of the evidence is to show that the insoluble albumose is formed from the soluble. Moreover, I think that the globulin is transformed into the gluten-fibrin, for I have been able to obtain from the globulin in solution a body having the same reactions as the gluten-fibrin." What this evidence is, which, by its direction, shows that the insoluble albumose is derived from the soluble, is not clear, and Martin makes no further statements on this point. That a body should be obtained from the solution containing the globulin which had the same reactions as the "gluten-fibrin" is not surprising, for the so-called "albuminates" derived from nearly all globulins have no characteristic reactions, being merely soluble in dilute acids and alkalies, and precipitated by neutralization in the same way as "gluten fibrin." Martin then states his theory of the formation of gluten in the following scheme:

$$\text{Gluten} = \begin{cases} \text{Gluten-fibrin} & \text{—precursor, globulin.} \\ \text{Insoluble albumose} & \text{—} \quad \text{“} \quad \text{soluble albumose.} \end{cases}$$

This can not be a correct representation of the formation of gluten, for it has been shown to be founded on two erroneous observations: First, that alcohol does not extract proteid matter from the flour when applied directly, and second, that at least one-half the proteid matter of the seed is a myosin-like globulin.

The results obtained by us, and described at length in our paper,[1] lead to the conclusion that no ferment action is involved in the formation of gluten; that but two proteid substances are contained in the gluten, gliadin, and glutenin, and that these exist in the wheat kernel in the same form as in the gluten, except that in the latter they are combined with water in an amount equal to about twice the weight of the water-free proteids. The reasons for this opinion are, first, that alcohol extracts the same gliadin in the same amount, whether applied directly to the flour, to the gluten, or to the flour previously extracted with ten per cent. sodium chloride solution; second, that 0.2 per cent. potash extracts glutenin of uniform composition and properties from flour which has been extracted with alcohol or with ten per cent. sodium chloride brine and then with alcohol, as well as from gluten which has been exhausted with alcohol.

Both glutenin and gliadin are necessary for the formation of gluten, as shown by the three following experiments:

1. A portion of flour was washed completely free from gliadin by means of alcohol of 0.90 sp. gr., next with stronger alcohol, finally with absolute alcohol, and air-dried. The residue was then rubbed up fine until all lumps were removed, and water carefully added, and a dough made of the mass. A tolerably coherent dough was thus obtained, but much less elastic and tough than that produced from the untreated flour. This dough was then washed with water on a sieve, using every precaution to obtain a gluten, but none was formed.

2. Again, 7.5 grams of very finely ground air-dried gliadin were mixed intimately with seventy grams of fine corn-starch and distilled water added. A plastic dough was thus produced, but it had no toughness. On adding a little ten per cent. sodium chloride solution, the dough became at once tough and elastic. This was then washed with great care on a sieve with cold water,

[1] *Am. Chem. J.*, 15, 392–471.

a little ten per cent. salt solution being added from time to time, but in spite of every precaution no gluten was obtained.

3. The following experiment shows that the gliadin used was capable of forming gluten when glutenin was present, and also that salts have a marked influence on the toughness of wheaten dough.

Two portions of flour, weighing 100 grams each, were taken, and after adding five grams of gliadin to one, both were made into dough with the same quantity of water. The two doughs presented marked differences; that to which the gliadin had been added was much tougher and more yellow than the other. They were then washed with water as long as starch separated. The gluten was dried superficially by wiping with a cloth and weighed in the moist state. That from 100 grams of flour to which five grams of gliadin had been added weighed 44.55 grams; that from 100 grams of flour alone weighed 27.65 grams. The moist glutens were dried at 110° to constant weight, and both yielded the same proportion of dry gluten; *viz.*, 34.6 per cent. The yield of dry gluten was accordingly, in the first case, 15.41 grams, and in the second, 9.56 grams. The difference, 5.85 grams, shows that the added gliadin was fully recovered in the gluten.

The above figures show that these proteids combine with about twice their weight of water in forming gluten. The fact that the added gliadin entered so readily and completely into the formation of gluten indicates that it exists in the seed as such and undergoes no chemical change during extraction and drying.

The properties observed in testing the separated gliadin show how it acts in forming gluten, and explain many of the points observed by others and attributed to a ferment action.

When treated with distilled water in small amount the fine ground air-dry gliadin at once forms a sticky mass which, on adding more distilled water, dissolves to a turbid solution. If, however, a very little sodium chloride is added to distilled water and this applied to gliadin that has been first moistened with pure water, a very coherent, viscid mass results which adheres to everything it touches, and can be drawn out into long threads. If the gliadin is moistened with ten per cent. sodium chloride

solution and then treated with a larger quantity of this solution, the substance unites to a plastic mass which can be drawn out into sheets and strings, but is not adhesive. From this it is evident why Ritthausen, in washing flours which gave a fluid gluten, obtainable only in small quantity and with great difficulty, found that the addition of calcium sulphate to the wash-water rendered the gluten much more coherent and easily obtainable. The gliadin is thus proved to be the binding material which causes the particles of flour to adhere to one another in forming a dough.

But the gliadin alone is not sufficient to form gluten, for it yields a soft and fluid mass which breaks up entirely on washing with water. The insoluble glutenin is probaby essential by affording a nucleus to which the gliadin adheres and from which it is not mechanically carried away by the wash-water.

It might be supposed that this insoluble glutenin, which so nearly resembles gliadin in composition, results from an alteration of the latter, brought about by the action of the mineral or other constituents of the seed or of the water. This is not probable, for the same amount of gliadin is extracted from flour directly by treating it with alcohol of 0.90 sp. gr., as is obtained from the gluten itself, and also the same amount is obtained after extracting the flour completely with ten per cent. sodium chloride solution, and then with alcohol.

The behavior of the gliadin towards ten per cent. sodium chloride solution shows why no gluten was obtained by Weyl and Bischoff from flour extracted with this solvent. The gliadin had under these conditions no ahhesive qualities, and therefore was unable to bind the flour into a coherent mass. If, however, the salt solution is added in small quantities, and the flour kneaded and pressed, the particles are brought together and then adhere tanaciously.

DEGRAS.[1]

By Charles S. Bush.

IN this country, the term "degras" is generally applied to the grease or fatty matter recovered from the water in which wool has been scoured; in various portions of Europe, the term

[1] Read before the Rhode Island Section, January 25, 1894.

is employed not only in connection with grease extracted from the waste-water of wool-washing establishments, but also to designate the oil or fatty matter recovered at chamois-skin manufactories.

It is my intention at this time to call your especial attention to degras of the first named type, which, I may say, has but one source; namely, the water in which wool has been scoured.

The process of producing or manufacturing degras (or so-called wool grease) is, comparatively speaking, a simple one and may be described as follows: The soapy liquid remaining in the scouring tubs or machines, after the wool has been scoured, is run off into a large shallow tank or pond and allowed to settle; the greater portion of the grease rises to the surface, but more or less adheres to the dirt and other foreign matter and is carried to the bottom. From time to time, the material which has accumulated at the bottom of the tank or pond is removed, and the grease, or a large portion thereof, is recovered. After the settling process is completed, the liquid is pumped into tanks and allowed to stand for a few days. The next step in the process is to add sulphuric acid. This withdraws the alkali used for washing the wool and breaking up the soapy emulsion, causes the grease and water to separate (this is commonly called "cracking the grease"). The contents of the tanks are then transferred to filter beds where the water is allowed to drain off, the grease and sediment being left behind in the filters. The filter beds may be composed of sawdust or other suitable material. The substance remaining in the filters is then transferred to pieces of bagging and shaped into flat packages. A large number of these packages are placed in power presses and steam applied in order to raise the temperature sufficiently to cause the grease to ooze out and flow into tanks provided for the purpose. Any water which may find its way into the presses will naturally pass into the tanks with the grease, but separation takes place at once and the hot degras, forming a layer on top, is readily drawn off into the barrels. After the degras has been allowed to cool, it is of about the consistency of soft tallow, and in such form is ready for market.

The color of the substance under consideration is yellowish-

brown; it has a disagreeable odor which is not easily described. This odor is due to two causes; first the presence of foreign substances, as dung and urine products, which are still present while the grease is being melted; second, the presence of certain volatile fatty acids which were present as potash salts in the wool, and, being soluble in the grease, remain with it after treatment of the emulsion with strong acid.

The individual character is given to wool grease by an interesting substance called cholesterin, the chemical formula of which is $C_{26}H_{44}O$. This substance is soluble in hot alcohol but precipitated in cold, in the form of tabular crystals somewhat resembling silver nitrate. As the extracted wool grease does not precipitate in the crystalline form, I think it is fair to infer that the cholesterin exists in the wool fat chemically combined with the fatty acid, and not in a state of mixture. Cholesterin is not saponifiable but it makes a most perfect emulsion, taking up 120 per cent. of water and remaining in that emulsive state for years; a sample in my possession is three years old and still shows no signs of separating.

Degras finds its chief use in the finishing of leather, superseding tallow for that purpose to a great extent, on account of the low price of the former and because of its penetrating and emollient nature. Degras is used to some extent in the manufacture of wool-oils, rope-oils, etc. Many persons have been led to believe that this waste material, which has polluted our streams and formed a subject for much discussion, is used extensively in the manufacture of soap. Some months since, an article appeared in one of our local newspapers from which I quote the following words: "In regard to finding a market for this material, I think it possible to sell it to almost any soap manufacturer. A large business is done in New York in this, and at a price of 2 to 2½ cents per pound." To say the least, this newspaper statement is misleading. Degras has been used to a slight extent by a few soap manufacturers but the results have been anything but satisfactory. Cholesterin is unsaponifiable and a positive injury to the soap. It has no detersive properties, and is undesirable as a "filler." There is no doubt that new outlets for this interesting product will be discovered eventually.

THE BORIC ACID WORKS AT LARDARELO.[1]

By Wm. P. Mason.

SO far as I am aware no recent description of these famous works has been given, and there is certainly wide-spread ignorance as to the best route by which to visit them. The most convenient starting point is Pisa, whence a train may be taken for Cecina at 6.10 A. M.

At Cecina one must change cars for the branch line going to Volterra. At Volterra station (not the town of that name, which lies some five miles away) a comfortable one-horse wagon, holding two besides the driver, may be hired for the round trip for ten francs. The regular post is to be avoided as it does not go far enough. The drive to Lardarelo will take two and a half hours, and the return journey will take about the same time. An evening train leaves Volterra station for Pisa. An attempt to pass the night *en route* would be attended with discomfort and is not recommended.

Unless the visitor be able to speak Italian an interpreter would be absolutely necessary.

The scenery between Volterra and Lardarelo, although hilly, can hardly be termed mountainous; and the soil, though poor in quality, is cultivated, olive plantations being seen in plenty. Altogether, the description of the approaches to the place, as depicted by the older authors, savors of a much more grim locality than the valley seen by the traveler of to-day—its infernal characteristics sink into nothingness when compared with the Yellowstone Park.

The dark color of the masses of friable serpentine on the hillsides, during the last mile of the drive, is the only reminder of the scenery as described by Muspratt, but wherever this rock occurs it does certainly give the surroundings "the appearance of having been burned."

Upon crossing a ridge within half a mile of the end of the journey, the boric acid plant, and its attendant village, suddenly come into view, and, with the numerous jets of native steam

[1] Read at the Baltimore Meeting, December 28, 1893.

rising from and among the buildings, the resemblance is very strong to a busy New England factory town.

All of the district now covered by the works was originally owned by the people of the neighboring ancient town of Monte Cerboli, but having been held by them as of little value, it was very cheaply obtained in 1818 by a poor young Frenchman (grandfather of the present Count Lardarel) who detected the presence of boric acid in the steam and who was shrewd enough to appreciate the value of his discovery.

He at first formed a company for the purpose of developing the property, but later acquired entire possession himself.

The boric acid, to the extent of one-tenth of one per cent., is contained in the native steam that issues from the earth through numerous orifices, all of which have been tubed to a greater or less degree.

These tubings are mostly of eight-inch pipe, and extend into the earth varying distances, some a few feet and others over three hundred. Certain of the fumaroles are entirely artificial, having been bored after the manner of artesian wells. The boring tool, when it reaches the steam zone, usually drops suddenly a yard or more, and immediately thereafter steam escapes with much force. The temperature of the issuing steam varies in the different outlets from 98°–140° C., and it rushes from the pipes with great noise and power.

Ordinary spring water is led into a circular brick cistern about thirty feet in diameter, and an eight-inch pipe, conducting natural steam passes through the cistern wall about one foot below the water surface.

The issuing steam, which impregnates the water with boric acid, causes a fountain of several feet in height to play in the cistern.

After an interval of twenty-four hours the contents of this cistern are piped into another similar one on a lower level, and are then subjected to a further injection of steam for an additional twenty-four hours, after which the solution passes to a square settling basin where a grayish mud, of exceedingly fine state of division, separates.

This mud, which contains more or less boric acid, is given

away to the country people who use it as an application for diseases of the hide occurring among sheep and cattle.

From the settling tank the boric acid water passes to evaporating pans (forty in number) made of lead. These pans are six feet wide, 150 feet long, and eight inches deep. They are slightly inclined, and are divided by small ridges two and a half inches high crossing them transversely every two feet. The liquid enters at one end and slowly flows over the step-like divisions to the other, the rate of inflow being made equal to that of evaporation.

When, in the judgment of the attendant, the concentration has been carried far enough, the flow is cut off and the hot, concentrated liquor is brushed out by brooms into crystallizing tanks, ten by thirty feet in size, and allowed to cool.

The deposited crystals of boric acid are removed by wooden scoops, drained in baskets, and the mother liquor is returned to the evaporating pans.

The crystals are spread upon a steam-heated drying floor protected by a shed-like building thirty by fifty feet in area, and when dry are placed in bins for storage. Shipment is made in casks holding about 1,000 pounds each. The heating of the evaporating pans and drying floor, in short heating of every description throughout the establishment, is by native steam.

About 200 hands are employed in the works, and the annual output is approximately 1,700 tons, all of which is shipped to England, *via* Leghorn.

Count Lardarel appears to have a careful eye for the welfare of his employees, as is evinced by the substantial manner in which the village is built, its cleanliness and the attempts made to adorn the streets. He was awarded a medal at the Paris Exposition for his contributions towards the betterment of social conditions, in addition to an award made for his manufactures.

The statement in our standard works of reference that "boric acid is recovered at both Monte Cerboli and at Lardarelo," is confusing, as they are practically one and the same place; and the dimensions given the artificial lagoons, "100 to 200 feet in diameter," is a great exaggeration.

RENSSELAER POLYTECHNIC INSTITUTE,
May, 1894.

THE COMMERCIAL VALUATION OF LEAD-TIN AND LEAD-ANTIMONY ALLOYS.[1]

By Joseph W. Richards, Ph.D.

LEAD-TIN alloys are used principally as soft solders, for coating terne plates and making "tin-foil." The amounts used annually for these purposes in this country may easily amount to twenty or thirty thousand tons, valued at some five million dollars. Since lead is worth about five cents a pound, and tin about twenty, the percentage of the latter fixes the value of the alloy; and since dishonest manufacturers are constantly trying to "cut grades" by shaving down the proportion of tin, consumers are constantly on the alert to detect such frauds. A quick, easy method of determining approximately the percentage of tin in such alloys becomes a valuable desideratum in such important industries. Accuracy to one per cent. is amply sufficient for all commercial purposes, because alloys conscientiously made by a careful manufacturer will vary that much from what they are intended to be if made by simply mixing given weights of the two metals.

Lead-antimony alloys, or hard lead, run up to twenty-four per cent. of antimony. Many thousand tons of this is used annually in the type-metal and britannia-ware industries, the proportion of antimony varying usually between five and fifteen per cent.

The commercial testing and valuation of such alloys can be most conveniently and quickly accomplished by determining their specific gravities. Pure lead has a density of 11.33, pure tin 7.43, and antimony 6.65. When tin is added to lead, the density at once falls; not uniformly, however, and the alloy, furthermore, does not have a density such as could be calculated from that of its component metals. It is the same on adding antimony, except that with one per cent. the alloy is *heavier* than lead, with two per cent. it is just the density of lead, and above that figure the gravity decreases as with tin. Over twenty-four per cent. of antimony, no homogeneous alloy can be obtained, and this sets a limit to the specific gravity tests; however, twenty

[1] Read before the Lehigh Valley Section, May 3, 1894.

per cent. may be regarded as the maximum ever found in commercial "hard lead."

To inaugurate this scheme of testing, it is necessary to carefully make the whole series of alloys, every one or two per cent. from pure lead to pure tin, and from pure lead up to twenty-four per cent. of antimony. Having determined the specific gravity of these alloys by the time-honored scheme of weighing in air and water, with a good balance, the results are tabulated, and any commercial alloys similarly treated and referred to it are at once identified. This method, however, requires a delicate balance and a careful operator; in fact, rather more skill than an ordinary metal-handler possesses. The apparatus shown in the accompanying cut was devised by Mr. Joseph Richards, of the Delaware Metal Refinery, Philadelphia, to facilitate these tests. The idea is to cast a bullet of fixed size in a brass mould, with each of the standard alloys, and then to weigh the bullets on a delicate scale. The scale shown has agate bearings, and the long beam is graduated every one per cent. from 0–pure lead, to 100–pure tin. On the reverse side, the beam is graduated from two up to twenty-four for the lead-antimony alloys. The marks on the beams have all been fixed by placing on the pan successively bullets of the standard alloys, and marking their weight.

The operation of testing a lead-tin or "hard lead" alloy thus resolves itself into simply melting it in a small iron ladle, pouring

the bullet and placing it on the scale; on balancing, the percentage of tin or antimony is read off directly on the beam. The balance is delicate enough to rise or fall with a movement of less than one-half of one per cent., while, with care, duplicate bullets may be cast not varying in weight over one-half per cent. The only precautions to observe are to continue the pouring until the bullet is set, in order to avoid a shrinkage cavity, and not to pour into a hot mould, which would necessarily be larger and cast a heavier bullet. The whole operation of melting, casting, and weighing can be performed easily in three to five minutes, and, if need be, by any workman of ordinary intelligence.

Nearly a score of these outfits have been sold by Mr. Richards during the last six months, and their introduction into the industries using these alloys has displaced the rule-of-thumb practice by accurate calculation, and brought many a dishonest manufacturer to his proper deserts.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.[1]

By Walter D. Field.

PART III.

(*Continued from p. 498.*)

THE peculiar form in which pyroxylin is deposited from its ether-alcohol solution, first called the attention of experimenters to it as a means for producing improvements in the various industrial arts. Photography was the first of the industrial arts to utilize this peculiar property of soluble nitrocellulose.

Later English experimenters made attempts to use pyroxylin as the base for an imitation bone, ivory or hard rubber. Parks, Spill, Greening, and others labored industriously to find some way or some solvent that would dissolve pyroxylin so they could obtain it in solid blocks suitable for turning and molding.

Four years after Scott Archer used pyroxylin in photography, Parks filed his first patent for the use of a solution of pyroxylin: (Eng. Pat. No. 2359, Oct. 22, 1855.) Then again in May, 1858 (Eng. Pat. No. 1090), John MacIntosh proposed the use of pyroxylin dissolved in a solvent, composed "of equal parts of wood spirit and coal naphtha" for use in the insulation of wire. In 1864 Parks (Eng. Pat. No. 2675) proposed the use of pyroxy-

[1] Read before the World's Congress of Chemists, June, 1893.

lin with gum ballata and says: "I employ as a solvent which I prepared by distilling wood naphtha with calcium chloride." Parks seems to recognize the desirability of using a solvent as near anhydrous as possible, and says the greater the quantity of calcium chloride used the stronger the solvent. But because of his solvent Parks was unable to make his experiments successful, and so he begins to search for solvents that would not evaporate so quickly and would enable him to work the pyroxylin solution in heated rolls. Parks finds that nitrobenzene, aniline, glacial acetic acid, and camphor dissolved in the more volatile solvents, methyl alcohol and alcohol-ether are much better for use in producing a plastic as they are less volatile and develop greater solvent action under the influence of heat.

Spill (Eng. Pat. No. 3102, 1869) finds camphor in alcoholic solution, camphor oil, aldehyde alone or with alcohol, solvents of pyroxylin. Ethyl and methyl acetates were found to be solvents of pyroxylin by Pelouse (*Compt. rend.*, **24**, 2), and ether-alcohol by Dominte and Merard (*Compt. rend.*, **29**, 390). Acetone was known to be a solvent of pyroxylin prior to 1864. To the solvents already given none were added until 1882, when John H. Stevens took out a series of patents, in which he gives a large number of new solvents for use in the production of solid compounds of pyroxylin. In these patents (U. S. P. Nos. 269, 340, 269,341, 269,342, 269,344, 269,345,) he names the following substances: methyl nitrate, ethyl butyrate, ethyl valerate, ethyl benzoate, ethyl formate, methyl salicylate, amyl formate, amyl acetate, amyl butyrate, amyl valerate, ethyl sebacylate, ethyl oxalate, diamyl oxide, which are all active solvents of pyroxylin, that is they are solvents at the usual temperatures. He names dinitrobenzene and coumarin as latent solvents, that is, they are solvents at their melting points or when dissolved in alcohol. Stevens also finds acetal, amyl nitrate, and amyl nitrite in alcoholic solution to be solvents of pyroxylin at ordinary temperatures.

In 1889 Robert Shupphous took out a series of patents (U. S. P. Nos. 410,204, 410,205, 410,206, 410,207, 410,208, and 410, 209). He finds propyl and isobutyl alcohols with camphor active solvents, and the ketones, palmitone, and stearone in

alcoholic solution, also alpha and beta naphthol with alcohol, and anthraquinone (diphenylene diketone) in alcoholic solution. Iso-valeric aldehyde and its derivatives, amyliden-dimethyl and amyliden-diethyl ethers, Shupphous finds are active solvents of pyroxylin.

In 1892 August Sayer (U. S. P. No. 470,451) informs us that diethylketone, dibutylketone, dipentylketone, and the mixed ketones, methylethyl, methylpropyl, methylbutyl, methylamyl, and ethylbutylketones are active solvents of pyroxylin. Still later Leonard Paget (U. S. P. No. 494,793) finds that methyl-amyl oxide is a solvent but ethylamyl oxide (U. S. P. No. 494, 792) is not a solvent.

The solvents of pyroxylin can be divided into the following general classes: First, those which are solvents, without the aid of heat or solution in alcohol; second, those that are solvents when dissolved in alcohol. These solvents are those which also develop a solvent action when heated to their melting point in combination with pyroxylin.

We also find that chemically the solvents of pyroxylin can be grouped into classes as follows: Two of the monohydric alcohols; compound ethers of the fatty acids with monohydric alcohols; aldehydes; simple and mixed ketones of the fatty acid series. These classes include the greater number of the solvents of pyroxylin those not included are as follows: Amyl nitrate and nitrite, methylenedimethyl ether, ethidenediethyl ether, amyl chloracetate, nitrobenzene and dinitrobenzene, coumarin, camphor, glacial acetic acid, and mono, di, and triacetin.

Another division of the solvents of pyroxylin is necessary when we consider their properties. We find it necessary to divide the solvents of pyroxylin into two great classes according as they are hygroscopic or non-hygroscopic. To the first class belong acetone, methyl acetate, ethyl acetate, methyl alcohol, aldehyde, ethyl formate, propyl formate and acetate. These solvents when they deposit pyroxylin from their solution, also absorb water and this precipitates the pyroxylin in the form of a white cloud on the surface of the deposited film. In some cases this cloudiness extends entirely through the film and it is like chalk dust in appearance.

Dr. Guido Wolfram (*Dingler's Poly. J.*, **230**, 156,) says: "Pentanitrocellulose is soluble in acetone, acetic ether, and still easier in a mixture of the same with ethyl ether. The solution gives a cloudy layer (matte) or film on evaporation." The pentanitrocellulose was not the cause of the cloudy film, for if he had used anhydrous solvents and evaporated his solution in a chamber free from moisture he would have obtained clear films.

Wolfram says: "The solution of the tetranitrocellulose in acetic ether, acetone, and wood-spirit, wood-spirit ether, acetic ether, ether, and acetone ether, gave a hazy opaque layer—a proof that the obtaining of a vitreous layer depends not only on the substance but likewise on the kind of solvent used." If Wolfram had used alcohol instead of ether in combination with the hygroscopic solvents he would have obtained clear transparent or glassy films on the evaporation of the solvent by reason of the alcohol absorbing the water and preventing the precipitation of the pyroxylin.

All the non-hygroscopic active solvents of pyroxylin deposit it from solution as a transparent, glassy film.

The action of the various solvents towards pyroxylin is often very peculiar. Thus is the case of the alcohol-ether solvent, neither the ether nor the alcohol is a solvent yet when combined they produce an active solvent. Camphor when dissolved in alcohol produces a good solvent; on the other hand camphor dissolved in the ketones reduces their solvent action. Nitrobenzene gives a solution that is granular, it seems to merely convert the pyroxylin and not to dissolve it, on the addition of alcohol (distilled from lime) we have at once a solution, that is, the granular appearance disappears and the solution becomes homogeneous.

The acid mixture and the method of nitrating has much to do with the action of the various solvents. The influence of water (uncombined) in the acid mixture, the influence of the immersion temperature, and the effect of increasing the nitric acid and diminishing the sulphuric acid, all influence the solubility of the resulting product.

We will consider first the influence of mechanically mixed water on the solubility of the pyroxylin.

Starting with a mixture of eight pounds of nitric acid, sp. gr. 1.435, and sixteen pounds of sulphuric acid, sp. gr. 1.83, and one-twentieth part by weight of cotton, first add six ounces of water and immerse the cotton at 60° C. The cotton is finished in ten or twelve minutes, and when washed and dried is found to be very pulverulent, or rotten and dusty, and occupies a much smaller bulk than the non-pulverulent variety insoluble in methyl alcohol. This pyroxylin is very soluble in methyl alcohol and in all hygroscopic solvents, giving with them limpid thin solutions.

Again taking the same proportions of acids of the gravities as given above, and the same amount of cotton for nitration, and adding nine ounces of water, the temperature of the immersion this time being 65° C., we find the pyroxylin produced very much more soluble in methyl alcohol than that produced by the first formula. Also that all its solutions are more limpid or fluid.

In this formula we have the following amounts of water: Eight pounds nitric acid, sp. gr. 1.435, contains 2 pounds, $2\frac{2}{5}$ ounces water. Sixteen pounds sulphuric acid, sp. gr., 1.83, contains 1 pound, $1\frac{3}{10}$ ounces water. Nine ounces water added makes the total water in the acid mixture 3 pounds, $13\frac{8}{10}$ ounces.

Now if we took a weaker nitric acid that would contain the desired water, without addition, as in the following formula: Eight pounds nitric acid, sp. gr. 1.40, contains 2 pounds, $10\frac{4}{5}$ ounces. Sixteen pounds sulphuric acid, sp. gr. 1.83, contains 1 pound, $1\frac{3}{10}$ ounces. Giving a total of 3 pounds $12\frac{9}{10}$ ounces. We would naturally suppose that this formula, containing as it does within an ounce of the same amount of water as the first formula, would produce pyroxylin having almost identical solubilities with that produced by the first formula. The two formulas do not, however, produce pyroxylins having the same solubilities, using, of course, in nitrating, the same temperature.

The pyroxylin produced by the formula containing the mechanically added water, is very soluble in methyl alcohol and hygroscopic solvents, but only imperfectly soluble in non-hygroscopic solvents, for instance, the compound ethers. Whereas the pyroxylin produced by the second formula, containing no mechanically added water, is perfectly soluble in the non-hygroscopic solvents, and its solutions in the hygroscopic solvents

are inclined to be heavy. The nitric acid used in these experiments was water-white and free from any dissolved nitrogen oxides.

The pyroxylin made from the formula containing the mechanically added water yields a film that is very contractile, that is, when it is deposited from its solution on a piece of plate glass it differs from other pyroxylins in drying to a much smaller bulk.

It was, however, the fact that the non-hygroscopic solvents of pyroxylin would deposit it as a film having great strength and transparency that led to its use for producing a varnish which could be applied to brass and silverware by simply dipping articles in it. The person who practically applied these properties was Richard Hale (U. S. P., No. 471,422). Hale uses the following solvent: Amyl acetate, four volumes; petroleum naphtha, four volumes; methyl alcohol, two volumes; pyroxylin, four to five ounces to the gallon of solvent. In this case, Hale has used petroleum naphtha to hasten the drying qualities of the varnish, so that it would set on the article to be varnished before it had a chance to run off. It was, however, the non-hygroscopic character of the solvent that made the varnish successful when it came to practical application. This very formula, or one which is a very slight modification, is used to-day in the production of thousands of gallons of pyroxylin varnish.

The varnish made on this principle is also used for varnishing pens and pencils and it gives them such a superior finish that they command a higher price than those varnished with the ordinary varnish.

And now the last industry that has sprung up, because of the wonderful properties of pyroxylin when deposited from its solution in a non-hygroscopic solvent, is the production of photographic films, flexible glass we would call it, and really, what better name could we give it? Henry Reichenbach made the first application of the use of a solvent of pyroxylin. that was practically non-hygroscopic, to the production of a photographic film. In his patent, issued in December, 1889, Reichenbach gives a formula, but as this formula is no longer in use, from the fact of its being too largely composed of hygroscopic solvents, there is no need of producing it here. It has been due to the recognition

by experimenters, that by a suitable combination of solvents solutions could be produced that would flow fast or slow, set rapidly or slowly, and produce the varied products desired, that the industry has developed so rapidly.

Hyatt's discovery that a mixture of camphor and pyroxylin when heated could be worked like rubber was the beginning of the success of the celluloid industry. Hyatt discovered the latent solvent action of camphor.

RECENT WORK ON THE SUGARS.

By B. B. Ross.

Received May 14, 1894.

THE ESTIMATION OF INVERT SUGARS.

Bauman (*Ztschr. des Ver. f Rubenzucker Ind.*, **42**, 824) gives a new table, based upon the original table of Herzfeld, for the calculation of invert sugar percentages in solutions containing considerable proportions of sucrose. The table is quite similar to that of Herzfeld, but provides for the employment of only five grams of material instead of ten grams, as in the old table.

Ehrmann (*Bull. Assoc. Chim., France*, **10**, 537) describes a method for the indirect gravimetric estimation of glucose by means of the reduction of one of the double platinum chlorides by the copper suboxide thrown down by the invert sugar.

The suboxide, precipitated in the usual manner is brought upon the filter and washed thoroughly; the reduction of the precipitate is next effected by pouring upon the filter a small amount of a concentrated solution of potassium platino or sodium platinochloride, the red precipitate of suboxide being superseded by a black deposit of platinum.

After washing and igniting the residue, the amount of invert sugar corresponding to the weight of platinum obtained, can be readily calculated.

The author claims that this method is more rapid and easy of execution than the reduction of cuprous oxide in a current of hydrogen, and that it is also more exact, for the reason that the atomic weight of platinum is much higher than that of copper.

Nihoul (*Chem. Ztg.*, **17**, 500) refers to the gravimetric

method dependent upon the reduction of the copper suboxide in a current of hydrogen, and offers the objection that the process, though accurate, is both tedious and time-consuming.

The process of Holdefleiss, involving the oxidation of the cuprous to cupric oxide with nitric acid, is also noted, as well as the objection of Soxhlet that a loss occurs from the formation of basic copper nitrate and that an error is occasioned by the retention of copper in the filters. The author reports results of tests refuting the first claim of Soxhlet and recommends the employment of double filters in order to obviate the slight error resulting from the presence of the small amount of copper retained in the filter papers. The inner filter containing the precipitate, and the outer filter are separately treated with nitric acid, ignited and weighed, the differences in the weights secured giving the weight of cupric oxide, and this multiplied by the factor 0.889 gives the amount of cuprous oxide corresponding thereto. From this the proportion of glucose can be readily obtained by reference to Allihn's tables.

Blank experiments with double filters showed that practically the same amounts of copper solution were absorbed and retained by each filter.

On account of the passage of small quantities of the suboxide through the first filter (as sometimes happens), it is recommended that quadruple filters be employed, the filters being ignited and weighed in pairs instead of individually.

By the observance of these directions, it is claimed that satisfactory results can be quickly and easily secured.

The author also reports the result of experimental tests of the gravimetric method which provides for the bringing of the suboxide upon tared filters, drying and weighing.

Two sets of double filters were employed in the filtrations, and in order to determine whether or not oxidation of the precipitate occurred during the drying process, some of the precipitated suboxide was maintained at a temperature of 75°–100° C. for two days without perceptible variation in weight.

It was found on investigation, however, that the precipitate obtained did not correspond precisely, in composition, to the formula Cu_2O, being contaminated to a slight degree with organic matter.

In following this method, which in other particulars is said to be highly satisfactory, it is therefore necessary to make a correction for the proportion of organic matter contained in the precipitate, this correction being generally about 0.3 to 0.4 per cent. of the weight of the cuprous oxide.

INVERT SUGARS IN THE BEET.

Classen (*Deutsche Zucker, Ind., 1893, Sucr. Ind.*, **41**, 242) recommends that in the estimation of invert sugars in the beet, the juice obtained by pressure from the beet be not employed and that, instead, the direct aqueous method of extraction be used in the preparation of the solution required for the determination.

For this purpose, the warm digestion process is found advantageous, a small amount of lead subacetate and precipitated calcium carbonate being previously added. Excess of lead subacetate should be avoided since this leads to the destruction of invert sugars, and on the other hand, if the juice has an acid reaction, inversion of sucrose will take place; the acidity, however, can be readily corrected by the employment of calcium carbonate.

The process recommended is as follows: Take 110 grams finely divided chips, add ten to fifteen cc. lead subacetate solution and one to two grams of precipitated calcium carbonate, digest in a half-liter flask on a water-bath from three-quarters to one hour. After cooling and making up to the mark, the moderately clear juice is decanted off and 100 cc. of it is measured out; a small amout of lead subacetate is next added to complete the clarification and the solution made up to 110 cc. and filtered. To 100 cc. of the filtrate a small amount of soda solution is added to precipitate the lead and the volume is then brought up to 200 cc. One hundred cc. of this liquid corresponds to ten grams of the beet pulp, and after it's filtration, the reduction of Fehling's solution can be accomplished in the usual manner.

LEAD SUBACETATE FOR CLARIFICATION.

Courtonne (*Bull. Assoc. Chim., France*, **10**, 457) refers to the chief methods proposed for the preparation of lead subacetate solutions and to the various formulas which have been assigned to this salt.

A series of tables is presented, giving densities of solutions of neutral and basic acetate, with the proportions of the solid salt, lead oxide and acetic acid contained therein, and showing also the relations between the two classes of solutions with reference to the amounts of acid and base present.

The author proposes the preparation of a basic acetate solution by adding to a solution of the neutral salt, an amount of ammonia sufficient to combine with such a proportion of the acetic acid of the lead acetate as will result in the formation of lead subacetate in solution along with ammonium acetate.

The proportions of the substances employed in the preparation of this solution are as follows:

Crystallized neutral lead acetate.....	350 grams.
Distilled water.....	825 "
Ammonia (22°).....	55 "

The author states that this solution has been employed by him for a long period of time and has given uniformly good results in the clarification of sugar solutions.

In addition to the tables above referred to, the author inserts an additional one giving data of a corresponding character for solutions prepared by the process just described.

THE INFLUENCE OF LEAD SUBACETATE UPON THE POLARIZATION OF CANE JUICES.

Saillard (*Bull. Assoc. Chim., France*, **10**, 354) reports results of a number of polariscopic tests of cane juices, where both normal and basic lead acetate were employed in the clarification.

Where the subacetate was employed the results were considerably higher owing to the formation of insoluble lead levulosate, thus decreasing the normal levo-rotary influence of the invert sugar present.

The author gives examples showing the effect of this difference upon the aggregate results for a whole milling season.

[Note by abstractor—Attention was called to this point a number of years since by Gill, Spencer, Edson, and others.]

THE INFLUENCE OF ALKALINE NITRATES UPON THE POLARIZATION OF SUGAR SOLUTIONS.

Gravier (*Bull. Assoc. Chim., France*, **10**, 351) reports a number of experiments which he has conducted in order to ascertain

the influence of alkaline nitrates upon the polarization of sugar solutions. The tests were executed with both aqueous and alcoholic solutions, and both in the presence and absence of lead subacetate.

In aqueous solution the influence of potassium and sodium nitrates was almost inappreciable, but in alcoholic solutions, in the presence of lead subacetate, there was quite a considerable diminution in the polariscopic readings.

The author concludes that it is inadvisable to employ alcohol as a solvent in polariscopic work, especially where lead subacetate is used.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE.]

THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL.[1]

BY W. A. NOYES AND E. D. FROHMAN.

Received June 18, 1894.

VERY full directions for the volumetric determination of phosphorus in steel have been recently given by C. B. Dudley and F. N. Pease.[2] The method is rapid and easy of execution and gives concordant results in the hands of careful workers. There is, however, an uncertainty of about ten per cent. as regards the factor which should be used for converting the iron equivalent of the permanganate solution into the phosphorus equivalent. The most careful determination of the character of the products obtained by reducing molybdic anhydride with zinc and sulphuric acid seems to be that of v. der Pfordten,[3] who finds that when solutions are reduced and titrated with but slight exposure to the air the molybdenum is reduced to a form corresponding to the oxide Mo_2O_3. If this is true one molecule of molybdic anhydride requires, after reduction, the same amount of oxygen for oxidation as three atoms of iron. If we assume, further, that the yellow precipitate contains twelve molecules of molybdic anhydride for one atom of phosphorus, it follows that

[1] The work here described was presented to the Faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science by E. D. Frohman.

[2] *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

[3] *Ann. Chem.*, (Liebig) 222, 155.

one atom of phosphorus is equivalent to thirty-six atoms of iron. The iron equivalent of the solution should, therefore, be multiplied by $\frac{31}{36\times56}$, or by 0.01538, to find the phosphorus equivalent.

Werncke,[1] however, claims that the molybdenum is reduced to a form corresponding to the oxide $Mo_{12}O_{19}$. This would give the factor 0.01628.

Blair[2] follows Werncke and gives factors which reduce to the one last given.

Dudley and Pease[3] assume the same ratio between molybdic anhydride and iron but a different and empirical ratio between phosphorus and molybdic anhydride. Their factors combined give the factor 0.01724.

Doolittle and Eavenson[4] give factors which, when reduced to the same form, give the factor 0.0160.

These facts led us to take up a study of the question in order to determine, if possible, the cause of the differences and what the true factor is.

We undertook first the determination of the form to which the molybdenum is reduced. For this purpose we intended to use known amounts of pure molybdic anhydride. On examining the molybdic anhydride on hand, which had been bought as chemically pure, we found that it contained considerable quantities of ammonia and also some sodium. On account of the difficulty of preparing the anhydride in pure condition we determined next to use sodium molybdate. This was prepared from the anhydride by dissolving in the calculated amount of sodium hydroxide and crystallizing the salt obtained from water. When dried over sulphuric acid *in vacuo* the salt contains two molecules of water of crystallization. This is completely expelled at 250°

0.5713 gram of the salt lost 0.0823 gram H_2O at 250°.
0.1710 gram of the salt lost 0.0249 gram H_2O at 250°.

		Found.	
Calculated for $Na_2MoO_4+2H_2O$:		I.	II.
$2H_2O$	14.88	14.40	14.56

1 *Ztschr. anal. Chem.*, 14, 9.
2 "Chemical Analysis of Iron," first edition, p. 86.
3 This JOURNAL, 16, 230,
4 Ibid, 16, 243.

The purity of the dry salt was further established by determining the amount of sodium in it by gentle ignition in dry hydrochloric acid as described by E. F. Smith and Philip Maas.[1]

0.3620 gram of the dry salt gave 0.2044 gram NaCl.

0.1148 gram of the salt gave 0.0648 gram NaCl.

		Found.	
Calculated for Na_2MoO_4.		I.	II.
NaCl	56.70	56.46	56.44.

For reduction 4.3405 grams of this sodium molybdate, dried at 250°, were dissolved in 200 cc. of water. Ten cc. of the solution, therefore, contained 0.1517 gram of molybdic anhydride.

The permanganate solution used was standardized by means of ammonium oxalate and of ferrous ammonium sulphate.

0.8923 gram of the ferrous ammonium sulphate required 17.88 cc. of the solution.

0.2077 gram of the ammonium oxalate required 22.93 cc. of the solution.

These results give respectively 0.007129 and 0.007144 as the iron equivalent of the solution, and one cc. of the solution contains 0.00102 gram of available oxygen.

For reduction ten cc. of the solution of sodium molybdate referred to above were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid (1 : 5 by vol.), and the solution was passed through the "reductor"[2] and followed by 100 cc. of dilute sulphuric acid (1 : 100) for washing. The solution was then titrated in the flask. In all the experiments a correction was made for the amount of potassium permanganate required in blank experiments with the same quantities of dilute sulphuric acid. The corrected values are given throughout this paper.

In the first experiments amounts of potassium permanganate were required which corresponded to from 15.90 to 16.35 per cent. of oxygen as compared with the amount of molybdic anhydride present. If reduced to the form corresponding to the oxide Mo_2O_3 16.67 per cent. of oxygen should be required, while for the form $Mo_{12}O_{19}$ but 15.74 per cent. is required. The results were not concordant and a little study of the matter led to the discovery that the reduced solution is very easily reoxidized by

[1] This JOURNAL, 15, 398.

[2] *J. Anal. Chem.*, 3, 123.

exposure to the air or by oxygen contained in water used for dilution. We have since found that Werncke states this fact very clearly in his paper,[1] but his statement seems to have been overlooked by recent workers and curiously enough Blair states almost exactly the contrary.[2]

The following illustrations of the ease with which the solution is oxidized may be given. A solution reduced as usual and which would have required at least sixteen per cent. of oxygen for its oxidation was poured into a beaker and back into the flask several times and then required only 14.89 per cent. of oxygen. A second solution reduced and then poured back and forth six times required only 13.74 per cent. of oxygen.

As it is evident from these experiments that the reduced solution must be titrated with very little exposure to the air, the reduction was next effected as follows: ten cc. of the sodium molybdate solution were diluted with 140 cc. of water and fifty cc. of dilute sulphuric acid. In the flask which was to receive the solution were placed two grams of acid sodium carbonate and five cc. of dilute sulphuric acid, thus expelling the air almost completely. A small amount of very dilute sulphuric acid was passed through the reductor first, then the molybdate solution as described and then 100 cc. of water containing five cc. of dilute sulphuric acid for washing. During all, care was taken to keep the reductor full and allow no air to pass through it. The reduced solution was titrated immediately *in the reductor flask*. Two solutions reduced in this way required respectively 24.8 cc. and 24.83 cc. of the permanganate solution, or 16.74 per cent. and 16.76 per cent. of oxygen.

The use of acid sodium carbonate for ordinary work would be somewhat troublesome and we next tried the effect of expelling most of the air from the reductor flask by passing through the reductor sixty cc. of dilute sulphuric acid (1 : 30) and following this with the solution to be reduced and the acid wash-water, taking care throughout that no air entered through the reductor tube. Ten cc. of the solution of sodium molybdate diluted with 140 cc. of water and fifty cc. of diluted sulphuric acid (1 : 5),

[1] *Ztschr. anal. Chem.*, 14, 7.

[2] "Chemical Analysis of Iron," p. 89.

required, when reduced in this way, 24.81 cc. of the permanganate solution, or 16.74 per cent. of oxygen.

Experiments were next tried with pure crystals of ordinary ammonium molybdate. This has the composition $(NH_4)_6Mo_7O_{24}+4H_2O$, and should require if the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3, 13.59 per cent. of oxygen for reoxidation; 0.2037 gram of the salt required, after reduction as last described, 27.48 cc. of the permanganate solution; 0.2025 gram of the salt required 27.32 cc. These amounts correspond to 13.76 and 13.76 per cent. of oxygen.

Some molybdic anhydride was next prepared by gently igniting in a porcelain dish a comparatively pure specimen until all ammonia was expelled and the substance had changed to a pure yellow color, 0.1722 gram of this anhydride required, after reduction as last described, 27.76 cc. of the permanganate solution and 0.1726 gram required, 28.23 cc. or 16.44 and 16.68 per cent. of oxygen.

These experiments prove conclusively that if the reduction is properly executed the molybdenum is reduced to the form corresponding to the oxide Mo_2O_3. The conditions are that the solution should be preceded by some dilute sulphuric acid so that most of the air in the reductor flask may be expelled before the reduced solution enters it, that the sufficiently dilute solution shall pass the reductor slowly[1] and be followed by the acid wash-water without allowing air to enter the reductor at the top, and that the reduced solution shall be titrated at once and *without further dilution*. The reduced solution should be of a pure green color and not olive-green.

After establishing the ratio between molybdic anhydride and iron for the permanganate solution there still remain two questions before we can consider the ratio between the iron and phosphorus as settled.[2] These are, what is the ratio between molybdic anhydride and phosphorus in the yellow precipitate, and is the precipitation of the phosphorus practically complete in the case of the small amounts usually present in a steel analysis?

[1] See Doolittle and Ravenson. This JOURNAL, 16, 241.

[2] The paper of Prof. S. W. Johnson (this JOURNAL, 16, 462) has appeared since this was written. The presence of aluminum or manganese in its precipitate would not affect the results of the volumetric method. Iron, if present, would affect the results and that point deserves a more careful study.

The fact that there are twelve molecules of molybdic anhydride for one atom of phosphorus has been so thoroughly established by different observers that it seems scarcely necessary to discuss the matter or even to cite authorities. The experiments of Dudley and Pease[1] can not be considered as having much bearing on this question when we consider the extreme difficulty of the gravimetric determination of such minute amounts of phosphorus and the facts with regard to the reduction of the molybdenum which have been considered above.

The question as to the completeness of the precipitation is more difficult but we believe it is best studied by the precipitation of solutions containing known amounts of phosphorus under conditions practically identical with those of the steel analysis.

A solution of sodium phosphate was prepared of such strength that one cc. contained 0.000102 gram phosphorus (determined by evaporating a measured volume of the solution, igniting and weighing the sodium pyrophosphate), three cc. of this solution were placed in a flask with five grams of ferrous sulphate, free from phosphorus (equivalent to about one gram of iron), nitric acid was added, then potassium permanganate, and the precipitation of the phosphorus was effected exactly as directed by Dudley and Pease. The precipitate, after washing, was dissolved and reduced as described in the first part of our paper. In duplicate experiments 3.08 and 3.0 cc. of permanganate were required, which gives 0.34 and 0.33 mgm. of phosphorus instead of 0.31 mgm. actually present, if we use the theoretical factor which we have deduced for the relation between iron and phosphorus. Dudley's factor on the other hand would give 0.37 and 0.38 mgm.

Determinations were also made of the phosphorus in three samples of steel containing known amounts of phosphorus which were kindly furnished us by Dr. Dudley. They are the same steels to which Dr. Dudley has already referred. We give the results of our analyses calculated by the theoretical factor obtained by multiplying the iron equivalent of the permanganate solution by 0.01538, and also by the empirical factor of Dudley and Pease.

[1] This JOURNAL, 16, 229.

	Gravity determination, Per cent.	Volumetric determination. By theoretical factor.	By factor of Dudley and Pease.
Steel No. 1.....	0.040	0.040	0.045
" "		0.040	0.045
" "		0.039	0.044
Steel No. 2.....	0.053	0.050	0.056
" "		0.052	0.058
Steel No. 3.....	0.032	0.029	0.032
" "		0.034	0.038
" "		0.032	0.036

It is evident that the theoretical factor gives results which agree closely with the gravimetric determinations while the results calculated by the empirical factor of Dudley and Pease are decidedly too high. The evidence that the precipitation of the phosphorus is practically complete is quite satisfactory. It will be remembered that steel No. 2 contains arsenic. Our results seem to indicate that the arsenic is not precipitated to an appreciable extent with the phosphorus.

If the theoretical factor for the ratio between the iron and phosphorous equivalents of a potassium permanganate solution shall be confirmed by other observers, as we feel confident that it will be, the volumetric determination will be placed on so firm a basis that, at least in the absence of arsenic, the results obtained by it must be considered as more reliable than those obtained by any gravimetric method now in use. This cannot be true so long as the determination depends on an empirical factor, for any empirical factor is likely to vary with the amounts of phosphorus present and would not be applicable to steels containing widely different amounts of phosphorus.

TERRE HAUTE, June 15, 1894.

THE ANALYSIS OF MALT.

BY TOM CROSSMAN.

Received June 18, 1894.

IN the JOURNAL for May, 1894, there is an article on the analysis of malt by Dr. Miller. As a few of Dr. Miller's statements are totally opposed by those who have given the chemistry of malt their life study, I feel justified in bringing before your readers the methods of analysis which are in use for the valuation

of English malts in all our large breweries. The methods being based on the splendid researches of O'Sullivan, Heron, Brown, Morris, and others. I am aware that for the English infusion mashing we require better malt than when practicing the German decoction system. No doubt the methods given by Dr. Miller would give satisfaction to those brewers working on the German principle; but I make bold to assert, that a malt tested by the methods given in the article referred to, would not give information to the brewer which would be of any great practical guidance to him.

Dr. Miller asks, "From the standpoint of the brewer, the largest consumer of malt, what are the most important points to be ascertained by the analysis of a malt?" He then gives them as follows:

1. Moisture.
2. Extract.
3. Diastatic power.
4. Acidity.

I may add that the above factors *do not* tell the brewer much; but when taken in conjunction with the following, the results give him information of the greatest possible value.

5. Ready-formed sugars, soluble in cold water.
6. The percentage of uncoagulable albuminoids, soluble in cold water.
7. The quantity of free maltose, malto-dextrins, and free dextrin, when the malt is mashed under standard conditions.
8. The amount of unmodified starch or steeliness.

With reference to No. 1, nothing need be said as far as the method is concerned; but no practical brewer would ever dream of using malt containing five per cent. of moisture. Malt having three per cent. is generally looked upon with suspicion if required for a stock ale. One per cent. is normal to a good well-cured, and properly stored article.

The determination of moisture does not in all cases give us the information whether the malt has been properly dried or not originally, since it might have gained the water during careless storage. No brewer of my acquaintance thinks of judging the price of malt by the amount of water it contains, since he

knows fully well that the increase in moisture means increased deterioration.

2. The extract is usually determined by English chemists by what is known as Heron's method.[1] It consists of mashing fifty grams of ground malt with 400 cc. of water at 68° C., and keeping the temperature of the mash at 65°–66° C. for one hour. Afterwards the mash is cooled to 15.5° C. and made up to 515 cc. (500 cc. water, 15 cc. for space occupied by grains). The gravity is taken and the extract calculated therefrom. The wort is reserved for the further analysis, 7.

Heron's method is one which has given great satisfaction, since it is possible to analyse the starch products and compare them with other malts, giving information which is very much appreciated by practical brewers. The method is, by far, preferable to that following the conversion with iodine.

As opposed to Dr. Miller's statement I find that the majority of ale brewers are more guided, when purchasing malt, by the *quality* of the extract, as determined by the tests I am enumerating, than by the *quantity*.

3. The diastatic capacity is best determined by Lintner's method, which gives us the amount of curing the malt has been subjected to. It must not be forgotten, however, that two malts, each having the same diastatic power, will not behave the same, even if mashed under identical circumstances, unless the starch in each is in the same state of friability or freeness. Since, if the one malt is hard and vitreous and the other is free, the diastase will have more "work" to perform in the former than in the latter; therefore, the relative amounts of free maltose and malto-dextrin will be quite different. This is a point overlooked by several, they thinking if malts contain a given quantity of diastase, all the starch conversions will be the same providing the temperatures are similar. This is not so. The estimation of the diastatic power is not of much use unless we know the condition of the starch as determined by 7 and 8.

4. The acidity needs no comment.

5. The percentage of ready-formed sugars convey to the brewer more information as to the quality of the malt than is generally

[1] The Polariscope and Its Application to Brewing, (*J. Soc. Chem. Ind.*, 7, 259–276).

supposed. If the amount is low it is evident that the barley has been insufficiently germinated. If the quantity is high (*i. e.* over seventeen per cent. calculated on the malt) brewers agree that the beer produced from such a malt will not be sound; it also goes to prove that the malt has been forced or too quickly grown on the floors at high temperatures.

6. The amount of uncoagulable albuminoids and the amount of ready-formed sugars seem to bear a relation to each other. Moritz[1] has published some very interesting experiments which go to prove that under conditions specially favoring the attack and transformation of starch into sugars, there is a similar specially active attack upon the original albuminoids, and an abundant transformation of them into soluble forms. He also publishes a number of analyses of malts, and in each case he gives the factor obtained by dividing the soluble albuminoids into ready-formed sugars. It is a most noticeable fact that this factor is either 6.3, or a figure closely approximating it. There is sufficient proof here to convict the most skeptical, that it is absolutely impossible for a chemist to estimate the value of malt without first determining, 5 and 6.

7. By the estimation of free maltose and malto-dextrins, we get the knowledge how the starch is converted into the different sugars. It supplies to the brewer more information than it is at first possible, by non-brewers, to conceive; since it informs him how the starch behaves at fixed temperatures and conditions, he can then, to suit the class of beer he is desiring to produce, arrange his mashing heat with a certain amount of reliability.

Dr. Miller says, "It has been claimed by some that the percentage of sugars formed, and the amount of proteids dissolved, is of importance in judging the character of malt." I claim that the amount of sugars formed is very important in judging the character of malt, provided all malts are mashed under standard conditions, as is done when using Heron's method. I am aware that the increase or decrease of the percentage of the various transformation products is entirely dependent upon the manner in which malt is handled in the mash-tub, *combined with the condition of the starch and the amount of diastase.* Therefore, if the

[1] Technical Brewing; a Report on the Chief Features, in the year 1893.

brewer gets information as to the amount of the various sugars a malt yields when mashed under known conditions, surely he has a sound foundation upon which he can base his ideas in guiding him in the manner which the malt should be handled in the mash tub. The amount of free maltose and malto-dextrin in a wort, determine, to a very large extent, the condition, flavor and attenuation of the resultant beer. I cannot sufficiently emphasize the great importance of these determinations to the practical man.

8. The amount of unmodified starch or steeliness.

This a test of some significance, but not generally practiced. Its advantages are that it gives us the amount of unmodified or vitreous starch. It will be as well if I state the objects of malting, so as to better illustrate the importance and advantages of this test. The principal objects of malting are: The dissolution of the cellulose forming the cells in which the starch granules are enclosed, and the consequent liberation of the starch; the breaking down of the nitrogen constituents of the corn; the production of diastase for the future service in the mash-tub. Now, when the original barley is bad, or the malting has not been carried out on proper lines, the cellulose surrounding the starch granules is not dissolved, the starch is "locked up," so to speak, and in a very refractory condition making it well nigh impossible for the diastase to convert it at ordinary temperatures. A large amount of starch is then left in the grains, which may possibly get "semi-dissolved" and partly washed out by the subsequent higher sparging heats, and not being converted makes the production of gray or hazy beer very easy. If it were only a matter of dealing with steely malt we could surmount the difficulty by the decoction system of mashing; but it is understood that when the dissolution of the cellulose forming the cells is not satisfactory we have evidence of the glutens being only partly modified, and the resultant beers will not be as brilliant as those produced by a fully modified malt. Thus, a malt gives the best results in practice when the amount of unmodified starch, as estimated below, is small, providing other conditions are favorable. The following is the method I have used the last two years and have found exceedingly useful:

Fifty grams of malt are mashed, as in 2; the mash is then boiled very vigorously for one hour and afterwards cooled to 150° F. Fifty cc. of a cold water extract, previously prepared, as described below, are now added; the mash is kept at 150° F. for one hour longer. It is now cooled down to 60° F. and made up, as in 2, to 515 cc. The gravity is taken, allowance being made for the gravity added, *i. e.*, fifty cc. cold water extract. The difference in solid matter between boiled mash and mash, (2), will give the amount of unmodified starch. Example:

Boiled mash	77.0 per cent. solid matter,
Mash (2)	70.0 " " " "
	7.0 " " of unmodified starch.

The following is, in my opinion, the manner in which the results of malt analyses should be stated.

COMPOSITION OF WORT MASHED UNDER STANDARD CONDITIONS.

Free maltose, fermentable	33.30
Ready-formed sugars, fermentable	14.08
Malto-dextrins, unfermentable { maltose, 3.0 / dextrin, 1.9 }	4.90
Free dextrin, unfermentable	13.40
Albuminoids	2.21
Ash	1.60
Acid as lactic acid	0.51
Total dry extract	70.00
Unmodified starch	7.00
Moisture	1.90
Grains	21.10
	100.00

Diastatic capacity	30.
Color of wort	pale.
Flavor	good.

When the amount of unmodified starch exceeds much over seven per cent. it is sufficient to regard the malt with suspicion. A remarkable thing and an undisputed fact is, that beer made from a good foreign malt is more sound and brilliant than when made from good English malt. Yet, on comparing the analysis of each, we find that the unmodified matter, ready-formed sugars and soluble albuminoids, are smaller in amount in the foreign

than in the English malt. This speaks volumes for the value of malt analysis when conducted as described above.

NOTE.—Preparation of cold water malt extract. Fifty grams of ground malt are added to 500 cc. cold distilled water, and allowed to stand four hours with frequent stirring. It is then filtered absolutely brilliant, and used as directed.

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ON THE REACTION BETWEEN MOLYBDIC ACID AND POTASSIUM CHROMATE AND BICHROMATE.

BY ROBERT H. BRADBURY.

Received June 21, 1894.

MOLYBDENUM, as its position in the periodic system of the elements would indicate, offers many analogies with sulphur and more particularly with chromium. Thus, the most important acid of each is H_2RO_4, and the most stable acid-forming oxide RO_3. Again, sulphur and chromium have for some time been known to form a higher unstable oxide R_2O_7, and more recently a hydrated Mo_2O_7 has been prepared and investigated.

Potassium bichromate, $K_2Cr_2O_7$, is more fully written $K_2CrO_4CrO_3$, that is, it consists of a molecule of the neutral chromate combined with a molecule of chromic anhydride, and still higher anhydrochromates, *e. g.*, potassium trichromate, $K_2Cr_3O_{10}$ or $K_2CrO_4 2CrO_3$, have been shown to exist. The marked likeness between molybdenum and chromium led to the supposition that it might perhaps be possible to replace the chromium in potassium bichromate by molybdenum—that is, to obtain a compound $K_2CrO_4.MoO_3$. Since the bichromate results by the direct addition of chromic anhydride to the neutral chromate, it was supposed that the hypothetical chromo-molybdate might result by simple addition of molybdic anhydride to potassium chromate, thus

$$K_2CrO_4 + MoO_3 = K_2CrO_4.MoO_3.$$

At the suggestion of Dr. Smith I have investigated this subject, and while the result is not what was expected, it is of interest as adding another to the long list of facts which show that the rôle played by a substance in a reaction depends not only on the special qualities of the substance, but also to an equal degree on the amount in which it is present. The reaction which ensues when molybdic anhydride is brought together

with chromates has been investigated: A in the case of potassium chromate, B with potassium bichromate.

A. In determining the reaction of molybdic anhydride with neutral potassium chromate, the salt was dissolved in water and an equivalent quantity of molybdenum trioxide was added in small portions. Whether in the cold or in warm solution the molybdenum trioxide rapidly dissolves, the solution at the same time turning deep yellow-red in color. The molybdic oxide dissolves more rapidly when the process is executed in warm solution. The liquid was then slowly evaporated. At first there separated out from the solution a white mass. It was filtered, dried, and examined. It contained no chromium and was chiefly made up of unaltered molybdenum trioxide, perhaps with some potassium molybdate. The filtrate, which still retained its reddish-yellow tint, was evaporated. Further separation of the white material was constantly observed. From time to time it was again filtered off and the evaporation continued. At length a filtrate was obtained which was small in bulk and which apparently contained no more of the molybdic acid. In this, the reddish-yellow color which has already been referred to, was much deeper, corresponding with the increased concentration and showing that none of the colored material had been removed by the filtrations. This liquid was evaporated to crystallization and allowed to stand. The mass of red needles which separated was dried and recrystallized. This material was then examined. Under the microscope it did not differ from potassium bichromate, either in crystallization or in behavior toward polarized light. Analysis revealed the presence of but a trace of molybdenum and allowed no further doubt as to its nature.

The reaction between potassium chromate and molybdic anhydride therefore proceeds in the sense of the following equation:

$$2K_2CrO_4 + MoO_3 = K_2Cr_2O_7 + K_2MoO_4.$$

No direct addition takes place and no chromo-molybdate is produced. It follows from the fact that much unchanged molybdic anhydride separated out during evaporation and that the liquid contained a great deal of unaltered potassium chromate that the reaction is by no means quantitative. In fact the amount

of potassium bichromate formed is exceedingly small relatively to the quantities of potassium chromate and molybdic anhydride employed. Indeed we should expect from the position of molybdenum in the periodic system, from its higher atomic weight and from all the properties of its acid that the avidity of molybdic acid would be much less than that of chromic acid and therefore that the reaction

$$2K_2CrO_4 + MoO_3 = K_2Cr_2O_7 + K_2MoO_4$$

would not proceed very far before the stage of equilibrium would be reached in which the backward reaction

$$K_2Cr_2O_7 + K_2MoO_4 = 2K_2CrO_4 + MoO_3$$

attains the same velocity as the principal one and in which therefore the transformation ceases.

It would be possible, probably, to increase the quantity of potassium bichromate formed by increasing the amount of molybdic anhydride until a large excess of it was present, but no experiments in this direction have been made.

B. When molybdic anhydride is introduced into a solution of potassium bichromate in the cold no change appears to occur, but no experiments beyond a rough test have been carried out in this direction. The reaction which was investigated between potassium bichromate and molybdic acid takes place only at higher temperatures. Equivalent quantities of potassium bichromate and molybdic anhydride were mixed together and heated gently in a porcelain crucible. The mixture melts rather easily to a blackish-brown liquid and at the same time an effervescence, escape of oxygen, is noticed, which becomes more energetic as the temperature is raised. When the fusion became quiet the lamp was removed. On cooling, the contents of the liquid solidified to a brown mass, which was broken up and treated with hot water. Some unchanged bichromate was removed by this procedure and the insoluble residue was thoroughly washed and dried. It is a soft, loose powder of brown color. It was then subjected to analysis.

Hydrochloric acid dissolves most of it to a green solution, giving off chlorine. A small quantity of black residue remains which is not affected by nitric acid, or by nitric acid and potassium chlorate, or by fusion with sodium carbonate and sulphur.

On this account this residue was simply dried on a weighed filter and its weight deducted from that of the substance taken.

The process of analysis may be briefly described. The material was weighed out into a beaker, addition of sufficient strong hydrochloric acid to cover it was made and the heat of a water-bath applied. After complete decomposition, the residue, invariably slight in amount, was filtered off on a weighed filter and its weight deducted from that of the substance taken. The green filtrate was largely diluted with water and hydrogen sulphide passed into it for a long period. Molybdic trisulphide (MoS_3) precipitated. It was filtered on a weighed filter and its weight determined. An aliquot portion of the precipitate was taken and ignited in a Rose crucible in a strong current of dry hydrogen to convert it into molybdenum disulphide, MoS_2. The heat applied here must not be too high, or part of the material volatilizes yielding a black sublimate and loss of weight is the result. The molybdenum disulphide was allowed to cool in the current of gas and then weighed, and the quantity of molybdenum corresponding to the whole of the precipitate and therefore to the substance taken was found by the appropriate calculations. From the filtrate the chromium was precipitated as hydroxide by the addition of ammonia and was estimated in the usual way as sesquioxide.

The potassium in the filtrate from the chromium was weighed as usual, as chloride.

The results follow:

	A.	B.	C.	Mean.
Mo	43.69	43.56	43.17	43.45
Cr	14.71	14.65	15.00	14.79
K	11.08		11.86	11.47
Oxygen by difference				30.29

The formula $K_2O.Cr_2O_3.3MoO_3$ requires the following composition:

Mo	42.42
Cr	15.44
K	11.51
O	30.63

The compound in question is thus a basic molybdate of chromium and potassium.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

ACTION OF MOLYBDENUM DIOXIDE UPON SILVER SALTS.

By Edgar F. Smith and Owen L. Shinn.

Received June 15, 1894.

IT has been shown (*Ztschr. anorg. Chem.*, **1**, 360) that metallic molybdenum precipitates metallic silver from ammoniacal argentic solutions, but no record seems to have been made of the fact that molybdenum dioxide behaves similarly. This, however, was observed to be the case on introducing dioxide, prepared by the reduction of trioxide in a current of hydrogen, into an aqueous argentic nitrate solution for the purpose of learning whether any metal was present in the dioxide. All of the material dissolved on the application of a gentle heat. The solution was especially rapid in the presence of a slight quantity of ammonia. The silver separated in crystalline leaflets. Attempts were made to discover whether the reaction was really quantitative. The results are as follows:

1. 0.1057 gram brown dioxide, prepared by the reduction of ordinary molybdic acid in an atmosphere of hydrogen, precipitated from a slightly ammoniacal argentic nitrate solution 0.1755 gram metallic silver.

2. 0.1772 gram of dioxide precipitated 0.2915 gram of metallic silver. The latter was washed with dilute ammonia and with water.

Thinking that possibly the dioxide as prepared for the preceding precipitations did not really represent that oxide, but a mixture of oxides, recourse was had to a method first suggested by Manro and Pauebianco (*Gazz. chim. ital.*, **11**, 501). Muthmann (*Annalen der Chem.*, **288**, 116) employed this method with success. It is, briefly, the fusion of eight grams of dehydrated ammonium molybdate, seven grams of molybdic acid, fourteen grams of ignited potassium carbonate and seven grams of boric acid in a capacious and well-covered platinum crucible. The mixture should be held for several hours in a liquid condition. On cooling, a brittle mass results; it contains crystals of the dioxide. It can be readily detached from the crucible. The

brown oxide was purified by washing with ammonia water and then with pure water. The two reductions made with this oxide resulted as follows:

3. 0.3698 gram of oxide precipitated 0.6250 gram of silver.

4. 0.5287 gram of oxide threw out 0.8799 gram of silver.

In both cases ammonia, sufficient to precipitate silver oxide and again dissolve it, was added to the argentic solutions. The precipitated silver was also washed with ammonia water and finally with pure water.

If the ratio between the dioxide and the silver be deduced from the figures given in the preceding experiments it will be found to approach

$$1MoO_2 : 2Ag,$$

and then the calculated or theoretical quantity of silver required for the dioxide used in the various experiments would be

	Calculated Ag.	Found Ag.
1	0.1783 gram.	0.1752 gram.
2	0.2990 "	0.2915 "
3	0.6240 "	0.6250 "
4	0.8765 "	0.8799 "

The results in 3 and 4 agree more nearly with the theoretical requirements than those in 1 and 2, doubtless because the oxide used in those experiments was a true molybdenum dioxide. Their variation from the theory may be ascribed in 3 to slight solubility of the precipitated metal in ammonia, and in 4 to minute traces of molybdic acid in the silver.

Additional trials were made to arrive at more concordant results, but success was not achieved, although in every instance the resulting silver approximated the ratio previously established. This reaction, while apparently useless for quantitative purposes, is yet of interest as it shows that the precipitation of metallic silver is not confined to metallic molybdenum, but that it even extends to the dioxide and perhaps to other mixed oxides of which the dioxide may be a part.

It is of interest to note in connection with the conduct of molybdenum dioxide as outlined in the preceding paragraphs, the further analogy established between it and the dioxides of other metals of Group VI. Thus, tungsten dioxide reduces not only copper and mercuric salts, but also precipitates metallic

silver from ammoniacal silver solutions, and uranium dioxide, prepared by reduction of the oxalate in a current of hydrogen, dissolves in silver nitrate with the separation of metallic sliver. Molybdenum dioxide showed no reducing action upon copper and mercuric salt solutions.

Among the non-metals of Group VI we observe in the deportment of sulphites towards silver nitrate, in the breaking down of silver sulphite into metallic silver on the application of a gentle heat, a behavior analogous to that exhibited by molybdenum dioxide, and which we may consider as an additional contribution to the many already well-established analogies, existing among the derivatives of the elements constituting Group VI of the Periodic System.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

NEW BOOKS.

PRACTICAL INSTRUCTIONS IN QUANTITATIVE ASSAYING WITH THE BLOWPIPE. CONTAINING ALSO READILY APPLIED QUALITATIVE BLOWPIPE TESTS. BY E. L. FLETCHER. pp. 142. 14 Illustrations. Price, 12 mo. cloth, $1.25; morocco, $1.50. New York: John Wiley and Sons. 1894.

The manual of blowpipe analysis contains 142 pages with numerous cuts showing apparatus. It is well printed on serviceable paper and is of convenient size to be carried in the pocket.

Chapter I consists of descriptions of apparatus and general directions for their use, also in some cases the price of special appliances.

Chapter II is devoted to reagents, those commonly used in assaying, etc.

Chapter III contains descriptions of the various colored coats and flame tests given by the volatile elements.

Chapter IV describes the colored beads produced by all of the common and many of the rare elements when dissolved in borax or salt of phosphorus, both with the oxidizing and reducing flames.

Chapter V gives the method of reducing oxides on charcoal with soda.

Chapter VI. This chapter is the best in the book; here the ordinary qualitative blowpipe tests are distinctly and succinctly described.

Chapter VII, Quantitative assaying, describes in considerable detail the operations of sampling and of making quantitative blowpipe assays for silver, gold, lead, copper, tin, mercury, nickel, cobalt, and bismuth.

The appendix contains tables of hardness, atomic weights, etc.

A defect in the book is that the weights of ore are given in grains while the divisions on the scale, used for measuring the size and hence determining the weight of the buttons, reads milligrams, thus making calculations necessary which would be simplified by the use of the assay ton system.

In regard to the accuracy of the results obtainable by the methods described, granting that the button can be measured accurately to a cross-line of the scale, the differences are so great as to render the method nearly useless for ordinary gold ores. Cross-line No. 1=18 cents a ton in gold, No 2=$1.40 a ton, No. 3=$4.80 a ton, No. 4=$11.60 and so on.

The book may prove useful to prospectors, skilled in the use of the blowpipe, who have the good fortune to discover rich veins. E. H. M.

MINERAL RESOURCES OF THE UNITED STATES CALENDAR YEAR 1893. BY DAVID T. DAY, 8 vo. pp. v, 810, Washington, D. C.: Government Printing Office. Price 50 Cents.

This annual volume so well known to those interested in the mining industry carries forward the statistics to Dec. 31, 1893, and gives much descriptive matter to a later date. The following statements are of especial interest to chemists:

Aluminum.—"The total production of aluminum reached 333,629 pounds. * * It can be said that nearly all the steel makers use a small proportion of aluminum with the result of less waste in castings. For example, the amount of waste in crop ends on steel rails is lessened profitably. Ingot aluminum also goes to manufacturers of aluminum cooking utensils and this industry is extending satisfactorily. The remainder of the product goes out as sheet and wire for many purposes including

numberless experimental uses, among them lithographing with aluminum plates instead of zinc or lithographic stone. Some experiments in this direction in the map department of the Geological Survey indicate that the transfers obtained on aluminum are superior to those on zinc."

Salt.—"Notwithstanding the low prices which have prevailed and which have been due to keen competition among producers, there has been a laudable endeavor on the part of a number of manufacturers to improve the quality of their product. In this, signal success has been attained, and salt of American production has been so improved by new processes, which each producer holds secret, that importations of refined salt have almost ceased to be a factor in the industry. The competition in the production of fine grades of salt has become as sharp in its way as the competition in prices. Table and dairy salts are now prepared for commerce practically chemically pure—free from gypsum, calcium chloride, and magnesium salts."

Space will not permit of further extracts from this useful volume. E. H.

SEVENTH ANNUAL REPORT AGRICULTURAL EXPERIMENT STATION OF NEBRASKA FOR THE YEAR 1893. pp. 206. Lincoln, Nebraska: State Journal Co. 1894.

The volume includes brief statements of the work of the year by the director and the heads of the different departments, a list of books in some of the sections, the usual roster of officers and the financial statements. With these are bound nine articles which have already appeared as station bulletins and the title page of one other.

Chemists will be most interested in the two articles on the culture of the sugar-beet by Prof. Nicholson and his assistants, and in the article on the influence of changes of food and temperature on the quantity and quality of the milk of dairy cows.

The work on the sugar-beet is planned to cover the subject thoroughly, including culture, yields, richness of the beet, value of rejected portions, study of physiological problems, effect of fertilization, cost of production, seed production, and injury from insects.

Since Nebraska has become the second beet-sugar producing state in the union, parties interested in the subject naturally look to the bulletins of the Nebraska station for reliable information on the subject. They will find much important matter in this report. The work has been carried out on a larger scale than is usual in experiment station work. Under the head of fertilizers for beets it is stated that the use of "guano" seemed to be injurious to the beet. It is to be regretted that the actual composition of this "guano" is not given, as the "guano" now sold is often very different in origin and composition from the guano of standard reference books.

All the articles are fully illustrated by cuts, plates, and charts which add very materially to the interest and value of the volume. H. A. HUSTON.

ELECTRO-CHEMICAL ANALYSIS. By EDGAR F. SMITH. pp. 139, 27 illustrations. 2d Edition. Price $1.25. Philadelphia: P. Blakiston, Son & Co. 1894.

It is to Germany that we are accustomed to look for the scientific thoroughness which characterizes this little volume. Prof. Smith has long been known as an indefatigable worker in the field of electrolysis, and is a frequent and regular contributor to its literature. In this manual he presents, in clear and precise language, all that has stood the test of experience, and he deserves praise for avoiding to give undue prominence to his own methods. The very interesting chapter which he devotes to an historical sketch of the subject will doubtless serve to dispel erroneous notions that are entertained by many chemists regarding the authorship of certain methods.

In this new edition the character of the original work is preserved, but the additions show that the author has not allowed any recent publications of importance to escape his attention. Amongst others we note references to the interesting work of the Munich Polytechnic School, the valuable experiences of Elbs and of Oettel, and especially the excellent work that has been done in the laboratory of the University of Pennsylvania since the appearance of the first edition.

There is, no doubt, that we have here the most accurate, as well as the most complete work that has been written on electrochemical analysis. H. F. KELLER.

THE ALCHEMICAL ESSENCE AND THE CHEMICAL ELEMENT. AN EPISODE IN THE QUEST OF THE UNCHANGING. BY M. M. PATTISON MUIR. pp. 94. London: Longmans, Green & Co. 1894. Price $1.50.

This essay is a study "of the endeavors that men have made to give definiteness to the conception of unity of material phenomena" in the domain of chemistry. The discoveries and theories of the alchemists are summed up with no lack of appreciation, and the author proposes to judge the value of alchemical conceptions by finding "what results flowed from applying these conceptions to the study of nature." What, secondly, has chemistry accomplished by "examining material changes accurately and critically?"

The answers are given with dignity and fairness. The book is interesting; it seems intended for, and is adapted to the use of intelligent people who are not chemists, and contains home thrusts at some who are called "Modern Alchemists."

NINTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

CIRCULAR OF ANNOUNCEMENTS.

THE Ninth General Meeting of the AMERICAN CHEMICAL SOCIETY will be held in Brooklyn, N. Y., on Wednesday and Thursday, August 15th and 16th, 1894. The first session will be held at 10 A. M., August 15th, in room 42 of the Polytechnic Institute, No. 99 Livingston street. After the session, at 1.30 P. M., it is expected that a steamer will leave one of the wharves of the East river taking the chemists to the New York side where a lunch will be served at the mineral water establishment of Mr. Carl H. Schultz. After lunch there will be an opportunity to inspect the manufactory, and then the steamer will proceed to the U. S. Artillery School at Willet's Point, stopping at intermediate places of interest, and returning to Brooklyn in the evening.

The morning session on Thursday will begin at 9 A. M., and later in the day visits will be made to manufactories in the vicinity, returning in time for the address of Vice-President Norton before Section C of A. A. A. S., at 4:30 P. M.

Invitations have been received to visit various chemical establishments and places of scientific interest, and the local committee will arrange for such visits at convenient times during the two days appointed for the meeting of the American Chemical Society and the remaining days of the week, as the chemists who remain to participate in the meetings of the A. A. A. S. will undoubtedly be glad to avail themselves of such opportunities. The local committee of arrangements for the meetings of the A. A. A. S., and the other bodies which will be in session in Brooklyn at or near the same date, have secured for all of these organizations railroad rates of one and one-third fare for the round trip to Brooklyn or New York and return, under the following conditions:

(1) Each person, in order to secure said rates, must purchase a first-class ticket to Brooklyn or New York and pay full fare therefor, obtaining from the ticket agent a certificate to that effect upon a regular printed form. Such certificates will be available from August 10th—five days before the opening of the meeting. In case the agent at the starting point is not supplied with certificates or cannot give through tickets, the regular fare must be paid to the nearest station where such certificates can be obtained.

(2) These certificates must be deposited by holders, on their arrival at Brooklyn, with the Local Secretary, Prof. Geo. W. Plympton, who will return them when desired for the return trip.

(3) Before presenting these certificates at the ticket office in Brooklyn for obtaining return tickets they must be filled in on the back by the Local Secretary and also countersigned by the Special Agent of the Trunk Line Association. The Special Agent will be in attendance August 16th, 18th, 20th, and 24th.

(4) Certificates and return tickets are not transferable and the certificates will not be received by the Ticket Agents in Brooklyn after August 31st.

ALBERT C. HALE,
Gen. Sec'y of the American Chemical Society.

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AMERICAN CHEMICAL SOCIETY.

AN ATTEMPT TO PREPARE MOLYBDENUM HEXACHLORIDE.

BY EDGAR F. SMITH AND HENRY C. BURR.

Received June 15, 1894.

IT is well known that Teclu[1] obtained the hexachloride of tungsten by acting upon the trioxide of the metal with phosphorus pentachloride. The treatment of molybdenum trioxide in the same manner gave in one instance the compound $MoCl_5.POCl_3$ and in another, $MoCl_5.PCl_5$. In both of these derivatives the pentachloride of the metal is present. It would, therefore, seem that the metal is incapable of carrying the sixth chlorine atom. Reuter[2] heated both the trioxide of tungsten and that of molybdenum with silicon tetrachloride; his products, however, were not hexachlorides. Passing by his observations it was thought that if a partially chlorinated molybdic acid were exposed to chlorinating agents the residual oxygen might be removed and that then perhaps the hexachloride would be present in the reaction product. To this end molybdenyl chloride, MoO_2Cl_2, was mixed with an equivalent quantity of phosphorus pentachloride and heated in a sealed tube in the presence of chlorine to a temperature of about 170° C. On cooling, it was found that the tube contained a mass of greenish-black crystals, which when carefully freed from adherent phosphorus oxychloride by distillation in an atmosphere of chlorine gave a product that on analysis yielded figures approximating the pentachloride more closely than the hexachloride.

Silicon tetrachloride was substituted for the phosphorus pentachloride and the experiment repeated. The resulting crystalline

[1] *Ann. Chem.*, (Liebig's), 187, 255.

[2] Dissertation, Tübingen, *1893*.

product was quickly removed to a boat and carefully distilled in an atmosphere of carbon dioxide. Brown vapors were expelled from the boat, which finally contained nothing but white silica. The brown vapors quickly condensed in the colder portion of the tube, and upon analysis gave results varying between those required by the tetrachloride and pentachloride.

The conclusion to be drawn from these experiments then is that notwithstanding the molybdenum atom has already been partially chlorinated, and apparently is in a suitable condition to pass into the hexachloride, it yet does not do so, and we can hence only say that the molybdenum is either not sexivalent towards chlorine, or that at the elevated temperature at which these reactions took place, the hexachloride, if formed, cannot exist, but is dissociated into lower chlorinated derivatives.

On heating pure, finely divided molybdenum, intimately mixed with sugar-carbon, in an atmosphere of chlorine the invariable product was the pentachloride.

The temperature doubtless exerts a great influence in these reactions.

It has been observed in this laboratory that when metallic molybdenum acts upon an aqueous solution of ferric chloride rapid reduction of the ferric salt ensues with accompanying solution of the molybdenum. From a careful determination of the amount of iron thus reduced, the molybdenum evidently dissolves as a hexad, and it may be that if such solutions were allowed to evaporate slowly in desiccators, the hexachloride or some double salt, formed from it and ferrous chloride, might be found. Search will be made in this direction.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

THE ACTION OF HYDROCHLORIC ACID GAS UPON SODIUM VANADATE.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

Received June 18, 1894.

THE reaction of Debray[1]—the volatilization of molybdic acid by means of hydrochloric acid gas,—has suggested a number of experiments which of late have been tried in various

[1] *Compt. rend.*, 46, 1098.

directions in this laboratory. Among others we have exposed sodium pyrovanadate to the influence of the gas at temperatures ranging from the ordinary to about 440° C., and have found that it is possible in this manner to eliminate the vanadic acid from its salts.

In several experiments we used a preparation from Merck, marked "sodium vanadate." It was not white in color, but showed here and there spots that were yellow to reddish-brown. Weighed portions of this salt, after complete drying, were exposed in boats, to the action of pure hydrochloric acid gas. As soon as the boats were introduced into the gas the salt, *in the cold*, acquired a red-brown color. On the application of a gentle heat, vapors of similar color appeared over the boat and condensed in the colder, anterior portion of the combustion tube to a reddish-brown, semi-transparent, oily liquid, which was taken up by water with a brown color. In the boat remained sodium chloride, containing here and there minute black spots. On dissolving the salt, the black insoluble material was carefully examined and proved to be traces of vanadic oxide. They were undoubtedly present in the original salt and were the real cause of the reddish color noted in it. That they were not volatilized may be due possibly to the fact that they had previously undergone strong ignition, and were hence less volatile, although it was observed that by continued heating of the salt, while yet exposed to hydrochloric acid vapor, they gradually grew less in quantity. The results obtained in the four experiments, which follow, while they do not agree with the theoretical requirements yet show that the source of error was constant.

1. 0.0795 gram sodium vanadate gave 0.0546 gram sodium chloride, whereas if the salt analyzed had been pure sodium pyrovanadate it should have given 0.0606 gram sodium chloride.

2. 0.0786 gram sodium vanadate gave 0.0535 gram sodium chloride, instead of 0.0599 gram.

3. 0.1006 gram vanadate gave 0.0683 gram sodium chloride, instead of 0.0767 gram.

4. 0.1322 gram vanadate gave 0.0916 gram sodium chloride, while theory required 0.1007 gram.

Taking the purest vanadic acid that we could find, pyrovana-

date of sodium was prepared and obtained pure after several recrystallizations. The anhydrous material was exposed to hydrochloric acid gas as before with results that indicate a quantitative separation of the acid.

1. 0.1240 gram sodium pyrovanadate heated to 440° in hydrochloric acid gas gave 0.0935 gram of salt instead of 0.0945 gram.

2. 0.2197 gram sodium pyrovanadate gave 0.1669 gram sodium chloride, while theory requires 0.1672 gram.

The sodium chloride from these last two experiments was perfectly white in color, soluble without residue in water, and on examination showed no evidence of the presence of vanadium. The volatile product had the appearance of the compound $2VO_2.3H_2O.4HCl$ obtained by Berzelius when acting on vanadic acid with concentrated hydrochloric acid. If such be really the case we may suppose that in our reaction changes occurred similar to those indicated in the following equations:

$$\text{I. } Na_4V_2O_7 + 4HCl = 4NaCl + V_2O_5.2H_2O,$$

$$\text{II. } V_2O_5.2H_2O + 6HCl = 2VO_2.3H_2O.4HCl + Cl_2.$$

It will, however, be necessary to subject this volatile product to careful analysis before making a positive assertion in regard to its composition.

It is our intention to pursue this study further with the view of ascertaining whether by means of this reaction it will be possible to separate vanadic acid from certain of its associates from which it is now removed with difficulty. From the ease with which the transposition occurs we may hope that the atomic mass of vanadium may be determined after the same fashion as was done in the case of molybdenum.[1]

UNIVERSITY OF PENNSYLVANIA.

June, 1894.

ON SOME OF THE ARSENIC TESTS OF THE U. S. PHARMACOPOEIA (1890).[2]

BY CHARLES O. CURTMAN.

Received June 15, 1894.

NOTE.—In applying Bettendorf's test for arsenic, the Pharmacopoeia directs that to a small quantity of the liquid to be tested, which should contain much hydrochloric acid, or should be a solution of the substance

[1] *Ztschr. anorg. Chem.*, 5, 280.

[2] Report of the Pharmacopoeial Research Committee B.

to be tested in pure, concentrated hydrochloric acid, there should be added an equal volume of a saturated solution of freshly prepared stannous chloride in pure, concentrated hydrochloric acid, *together with a small piece of pure tin-foil.* The presence of arsenic is revealed by the production of a brown color or brown precipitate, the appearance of which is hastened by a gentle heat. By an oversight, the direction to add the tin-foil was inserted or left standing in the tests for arsenic in bismuth or antimony salts, in which it leads to false conclusion, as the following paper will show. (Dr. Chas. Rice, Chairman U. S. P. Revision.)

A NUMBER of experiments have been made for the purpose of ascertaining the conditions most favorable to the result of the test for arsenic by stannous chloride (Bettendorf's test and its modifications).

The inquiry was directed to the following points:

1. The limit of sensitiveness of the test in its various modifications.

2. The best proportion of reagent to specimen.

3. The influence of the use of metallic tin together with the stannous chloride.

4. The influence of the presence of other substances in the specimen tested.

I. Limit of Sensitiveness.

The following reagents were used:

a. The solution directed for Bettendorf's test by the U. S. P., consisting of a saturated solution of pure stannous chloride in pure, concentrated hydrochloric acid. The specific gravity of this solution was 1.407.

b. Metallic tin, perfectly pure, in thin cylinders, from which shavings of about 0.1 gram were taken as needed.

c. Stannous chloride solution prepared according to the German "Arzneibuch," by saturating a mixture of five parts of crystals of stannous chloride and one part of hydrochloric acid with dry hydrochloric acid gas. The specific gravity = 1.912.

All of the materials used were previously tested for absence of arsenic by Gutzeit's test, so as to exclude any fallacies arising from the introduction of even small traces of arsenic by the reagent, which might cumulate with those in the specimen.

It was easy enough to procure pure metallic tin, but impossible to obtain, from local dealers, hydrochloric acid sufficiently

free from arsenic to stand Gutzeit's test for one hour. So that I had to distill from purified sulphuric acid and pure sodium chloride the hydrochloric acid required for the preparation of the reagents.

A number of specimens of arsenic solution were made, containing free trioxide, sodium metarsenite and sodium arsenate in such proportion that each set corresponded exactly to an equal amount of As. They were:

Arsenic trioxide ($As_2O_3 = 197.68$), of which 1.31962 grams contain one gram of As.

Sodium metarsenite, ($NaAsO_2 = 129.82$), of which 1.7332 grams contain one gram of As.

Sodium arsenate, U. S. P. ($Na_2HAsO_4 + 7H_2O = 311.46$), of which 4.51834 grams contain one gram of As.

The solutions used for experiment contained from 0.5 gram to 0.01 gram of As. Of these, one cc. was used for each trial and the amount of reagent mixed with this varied from one cc. to three cc., so as to correspond with the limits prescribed in the pharmacopoeial tests. When metallic tin was added to the reagent, one cc. each of the specimen and the stannous chloride solution was used. In some cases of doubt a ten-fold quantity (10 : 30 cc. etc.) was used to obtain sufficient material for colorimetric comparison.

A uniform application of heat was effected whenever needed by imbedding the series of test-tubes under observation, to an equal depth, in a sand-bath heated to about 80° C.

Whenever comparisons of color became necessary to decide whether a deeper color had been produced than that of the unaffected reagent (as was especially necessary with the yellowish solution of the German pharmacopoeia), or whether a greater or less intensity of color characterized the reaction, narrow graduated cylinders of ten cc. capacity, were used in a dark box with light reflected from beneath, or occasionally for still greater accuracy, a pair of Hehner's colorimeter cylinders of 100 cc. capacity, also placed for observation into a dark box, admitting from beneath light reflected upward by a plate of milk-glass placed at an angle of 45°. With the aid of these appliances the following results were obtained:

a. With the U. S. P. solution of stannous chloride of sp. gr. 1.467, one cc. of each of the three specimens, containing 0.5 mgm. of As, was mixed in the different proportions stated below, and kept at ordinary temperature for one hour.

With one cc. of reagent a sharp reaction had taken place at the end of the hour. With two cc. of reagent the reaction was obtained earlier and was more intense at the end of one hour. With three cc. of the reagent the reaction was still more speedy, and at the end of the hour more intense.

No difference could be noticed either in time or in intensity between arsenic in the state of trioxide or pentoxide.

When the test-tubes were arranged exactly as before, but placed in hot sand, the time was somewhat shortened, and a slight increase of intensity noticed in all of the specimens.

b. When one cc. of the U. S. P. solution was used with one cc. of solutions containing 0.5 mgm. of As, and a small piece of metallic tin added and heat applied, the reaction was almost instantaneous, and in three minutes a very sharp, unmistakable coloration appeared which continued to increase in intensity for about ten or fifteen minutes, but was not notably darker at the end of the hour. No difference appeared in the different solutions containing arsenite and arsenate.

c. When from one to three cc. of the stannous chloride of the German pharmacopeia was used with one cc. of the solutions containing 0.5 mgm. of As, there was a slight darkening of the color in a few minutes, which continued to increase to the end of the hour. No difference was perceivable between the arsenous and the arsenic preparations. At fifteen minutes the specimens treated by the U. S. P. solution and metallic tin showed a much greater intensity of color, but toward the end of the hour there was but little difference perceptible between the color of the specimens treated with three cc. of the German reagent without heat, and that treated with one cc. of the U. S. P. reagent, metallic tin, and heat. The specimens containing less than 2.5 cc. of reagent showed a less intense color.

These experiments were repeated with the three solutions containing 0.05 mgm. of As. in one cc. and resulted as follows:

a. With the U. S. P. solution of stannous chloride: One cc.

gave no reaction during forty-five minutes, then gradual coloration began. If heat be applied the reaction begins in eighteen minutes and at the end of one hour is slightly more intense than when treated without heat. 1.5 cc. of reagent: reaction slightly more rapid and intense than with one cc. 2.0 cc. of reagent: still more rapid and intense, both with and without heating. 2.5 cc. of $SnCl_2$: reaction begins in fifteen minutes at air temperature in less than five minutes when heated. 3.0 cc. of $SnCl_2$: reaction slightly less intense than with 2.5 cc., both hot and cold. 3.5 cc. of reagent: a still further slight decrease in intensity. No difference could be observed in the reaction of As_2O_3 and As_2O_5; the sodium metarsenite appeared to be very slightly more colored than As_2O_5.

b. With one cc. of the U. S. P. solution and a small piece of metallic tin, at a temperature of about 80° C., one cc. of the solutions containing 0.05 mgm. of As, began showing a brownish color at thirteen minutes. At thirty-five minutes the reaction was quite sharp and continued to grow slowly in intensity to the end of the hour. No difference was perceptible between As_2O_3 and As_2O_5.

Three cc. of the solution of the "Arzneibuch" mixed with one cc. of the solutions containing 0.05 mgm. of As, began showing a feeble reaction at thirty-five minutes, and at the end of the hour showed a plain reaction as compared with the unchanged reagent, but did not equal in intensity, the reaction produced by the addition of metallic tin.

On repeating the experiments with solutions containing 0.03 mgm. of As in one cc., a feeble reaction resulted from the use of stannous chloride and metallic tin at the end of an hour, but even after standing over night the other methods gave such a faint reaction that it required close inspection in the colorimeter to perceive the change. A solution containing 0.02 mgm. of arsenic failed to show any reaction. So I think that for practical purposes the utmost limit of reaction is reached at 0.03 mgm. of As in one cc. and that the method employing metallic tin and heat is to be preferred where the presence of antimony or bismuth does not forbid its use. Even the addition of pure, concentrated sulphuric acid, which was recommended when the

test was first introduced, has not yielded to me any substantial advantage in detecting the presence of arsenic in greater dilutions.

II. The Best Proportion of Reagent to Specimen.

In the foregoing experiments and a number of others conducted for that purpose it was observed that both with the U. S. P. solution (without the use of metallic tin) and with that of the German pharmacopoeia, the greatest intensity of color obtained after an hour's reaction occurred when one cc. of the arsenical solution was mixed with 2.5 cc. of the reagent. Between three cc. and two cc. of the German solution hardly any difference could be found. But with the pale U. S. P. solution a very slight difference appeared in favor of two cc. as against three cc. Heat did not appear to affect the proportion needed.

When metallic tin was added it seemed to be best to use equal volumes of specimen and reagent, although the variable amount of dark coating of reduced arsenic adhering to the tin prevented an accurate comparison.

III. Influence of the Use of Metallic Tin Together With Stannous Chloride.

When metallic tin is heated with pure concentrated hydrochloric acid, a copious evolution of hydrogen results. When heated with the saturated solution of stannous chloride in hydrochloric acid, the evolution of hydrogen is but scant. When arsenic is mixed with the solution, the evolution of gas is perceptible but very feeble. Very little arsine appears to be evolved, for a paper cap with a drop of acidulated silver nitrate does not show any evidence of the reduction by AsH_3 for over fifteen minutes, and even at the end of an hour but a very faint arsenic reaction is seen.

To ascertain whether any of the arsine formed would react with the stannous chloride and thus hasten the reduction of As, I arranged a small apparatus in which a copious current of arsine, mixed with hydrogen, was generated and after passing through a bottle filled with dry cotton, was permitted to bubble through stannous chloride solution of the U. S. P. After more than an hour's time not a trace of coloration could be detected. So that after arsine has once been formed it is not again decomposed by

stannous chloride. Hence the prompt action of metallic tin must depend upon the *nascent* hydrogen, which aids the stannous chloride in reducing the trioxide and pentoxide.

But, however satisfactory the action of metallic tin in accelerating and intensifying the reduction of arsenic, it *cannot* be employed to detect arsenic in preparations of *bismuth or antimony*. For *the metallic tin reduces both of these metals*, and precipitates them from their solution as black floccules, which aggregate into small granular lumps. There could be a distinction made between the firm floccules of Sb or Bi and the finely divided brown particles of arsenic, but it would hardly be safe to trust to this appearance for a sufficient evidence of the presence of arsenic, and the preparations of Bi and Sb *must be tested without the aid of metallic tin*.

A number of specimens of pure bismuth and antimony salts were tested with the U. S. P. and the German solution of stannous chloride in various proportions. But neither at ordinary temperature nor when heated did the least coloring occur.

IV. Influence of the Presence of Other Substances in the Specimen Tested.

The preceding experiments were made with a solution of either arsenic trioxide or sodium metarsenite or arsenate in water, other substances being absent. But in testing various chemicals for traces of arsenic there are different conditions, as the arsenic forms only a very small portion of the mixture. In the U. S. P. the Bettendorf test is directed for eleven preparations. For hydrobromic, hydrochloric, phosphoric, and sulphuric acids, one cc. of the acid is to be tested by mixing with one cc. of the reagent, adding a small piece of tin-foil and heating. In case of magnesium sulphate, one gram of the dry substance is to be shaken with three cc. of the reagent; metallic tin is then to be added and an hour allowed for the appearance of the reaction; sodium phosphate, and pyrophosphate are treated in like manner, but heat applied and fifteen minutes time given.

In the case of antimony and potassium tartrate, antimony oxide, bismuth subcarbonate, and bismuth subnitrate, it was intended to test with stannous chloride alone for an hour, but by an unfortunate misunderstanding of the transcriber, tin-foil was

directed to be added, which will reduce Sb and Bi as well as As.

To find whether any of the chemicals directed to be tested by the stannous chloride method, could influence the detection of arsenic, specimens were prepared containing the pure chemicals shown to be free from arsenic by other tests, and with these small portions of arsenic were mixed and the tests compared with those in which arsenic was present in equal amount without admixture with the chemicals.

In no case could any difference in the intensity of the test be made out, nor were the differences in the time of the occurrence of the coloration sufficiently great or regular to justify the assumption that the reaction was impeded or accelerated by the presence of other salts.

ST. LOUIS, May 27, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY. No. 8.]

THE INFLUENCE OF ALUM, ALUMINUM HYDROXIDE AND ALUMINUM PHOSPHATE, ON THE DIGESTIBILITY OF BREAD.

BY W. D. BIGELOW AND C. C. HAMILTON.

Received June 28, 1894.

THE property which alum possesses of arresting the fermentation of flour, and making it possible to prepare presentable bread from very inferior flour has long been known, and the adulteration of flour by means of alum has been extensively practiced by millers and bakers. Comparatively little attention has been given to this subject in this country, but in Europe, especially in England, the question has been constantly before the minds of the public analysts for at least a quarter of a century. Indeed, as early as 1821 a law was passed prohibiting the addition of alum or any aluminum compound to flour or bread. This law remained in force till 1861 when it was repealed by the passage of a law which made it necessary for the prosecution to prove the injurious quality of the substance added.

It is universally admitted that the presence of alum as such not only impedes digestion but also exercises an injurious effect on the digestive organs. There is one phase of the alum question, however, to which a great deal of attention has been

given, both in this country and abroad; namely, the use of alum as the acid compound of baking powders. Unlike the practice of adding alum to flour or dough, this question has been attended with a long continued and fiercely contested controversy.

Many experienced analysts who have condemned alumed bread in unmeasured terms, have testified that in their opinion, bread baked with alum baking powders exercises no injurious influence on digestion or the digestive organs.

In the famous Norfolk[1] baking powder case, it was contended by the Government that alum united with the soluble phosphates of the flour with the formation of an insoluble compound, and that the flour was thus deprived of one of its most valuable constituents.

The defense, on the other hand, claimed that the aluminum was entirely precipitated as hydroxide. It is a curious fact that shortly after the Norfolk case the manufacturers of alum baking powders began the addition of acid calcium phosphate, and the position taken by prosecution and defense in the Norfolk case were reversed in a recent case[2] before the English courts. In the evidence submitted by the prosecution independent experiments were cited by Dunstan, Hehner, and Claude Thompson, to prove that aluminum hydroxide dried at 100° was soluble in two-tenths per cent. hydrochloric acid. Dunstan found aluminum hydroxide dried at 100° to be soluble in the gastric juice of a dog diluted to two-tenths per cent. of its normal strength, and that this fluid diluted to the same extent dissolved aluminum hydroxide from bread baked with the powder manufactured by the defendant.

Dunstan also found that aluminum hydroxide in bread interfered with the action of diastase (hence, with ptyalin, the digestive ferment of the saliva), and with peptic and pancreatic digestion. Also, that a three-tenths per cent. solution of sodium carbonate (the strength of the alkali in the intestinal juice) would dissolve aluminum hydroxide which had been dried at 100°. He also testified that he had found an aluminum salt in the urine of a man who had eaten one to two grams of aluminum hydroxide which had been dried at 100°.

Morgan testified that he had dissolved aluminum hydroxide

[1] *Analyst*, *1879*, 4, 231, and *1880*, 5, 21.

[2] *Analyst*, *1893*, 18, 152; *Chem. News*, *1893*, 67, 213.

which had been dried at 100° in his own vomit and in that of his son.

On the other hand, the defence took the ground that aluminum hydroxide was insoluble in the juices of the digestive organs. Sutton repeated Morgan's experiment, using as a dialyzer, however, a fresh sheep's bladder instead of a vegetable parchment as used by Morgan. Unlike Morgan he found no soluble aluminum compound in the dialysate. Luff cites an experiment intended to prove that dried aluminum hydroxide was insoluble in hydrochloric acid of the strength found in the gastric juice.

He took this strength of acid to be 0.02 per cent. instead of 0.2 per cent., the strength taken by the prosecution. His aluminum hydroxide also was heated to 150° instead of 100°, which is generally admitted to be the highest temperature attained by the interior of a loaf while baking, and he was not sure but the hydroxide might be changed to oxyhydroxide by heating to this temperature.

The work that has been done upon this subject seems to have been devoted to the influence of the gastric digestion alone, though J. West-Knights[1] and Dunstan,[2] working with diastase, reached the conclusion that the presence of alum, or of insoluble aluminum salts, interferes with the amylolytic action of ptyalin. Dunstan,[2] it is true, states that aluminum hydroxide interferes with pancreatic digestion, but appears to describe no experiment in proof of the statement.

J. West-Knights[1] found that gluten after treatment with alum, or its insoluble compounds, is about one-half less soluble in gastric juice than pure gluten, and pure bread is almost one-third more soluble than alumed bread in the same medium.

Pitkin[3] and Mallet[4] reached the conclusion that the aluminum compounds resulting from the use of alum baking powder were soluble to some extent in the gastric juice, while Patrick[5] found that when the dough was well mixed and bread well baked no aluminum hydroxide, resulting from the use of alum baking powder, was dissolved in the stomach of the cat. Hehner,[6] working

[1] *Analyst*, *1880*, 5, 67.
[2] *Ibid*, *1893*, 18, 152.
[3] *J. Am. Chem. Soc.*, *1887*, 9, 27.
[4] *Chem. News*, *1884*, 58, 276.
[5] *Analyst*, *1879*, 4, 207; from *Sci. Am. Sup.*
[6] *Analyst*, *1892*, 17, 201, and *1893*, 18, 213.

with an artificial pepsin solution, found the detrimental influence of alum baking powder to be equal to that of alum in the digestion of egg and bread.

The suggestion has often been made that the water-soluble salts resulting from the use of an alum baking powder, such as ammonium sulphate and potassium sulphate, would be more likely to retard digestion than the insoluble aluminum compounds. It was to study this question with reference to gastric digestion, but more especially with reference to double digestion with gastric and pancreatic ferments, that we undertook the work which forms the basis of this paper.

For the preparation of samples, flour was obtained which was known to be free from alum and seven two-pound loaves were baked under our direct supervision. The bread was raised in every case by compressed yeast.

As soon as the bread was baked it was cut in thin slices, dried at a temperature of 98°, ground, and bottled.

I. Digestion of Bread Free from Alum and Aluminum Compounds.

Loaf No. 1 was found to contain 12.06 per cent. of albuminoids. Portions of two grams each were subjected to several methods of digestion. The results given are the means of closely agreeing duplicate or triplicate determinations.

1. *Digestion in Pepsin Solution.*—The pepsin solution here employed is that suggested by Wilson in his modification of Stutzer's method.[1] One gram of Merck's granulated pepsin was dissolved in one liter of 0.33 per cent. hydrochloric acid. Two grams of the dried bread, which had been previously extracted with ether, were placed in a flask with 100 cc. of the acid pepsin solution, placed in a water-bath and kept at 40°, with frequent shaking, for twelve hours. The contents of the flasks were then filtered and the residue washed, dried, and kjeldahled. It was found that 93.26 per cent. of the total albuminoids in the bread were digested,

2. *Stutzer's Method.*—Two-gram portions of the bread were then digested according to Stutzer's method, except that an

[1] *J. Soc. Chem. Ind.*, 10, 118. See also Patterson in Report Maryland Experiment Station, *1891*.

artificial pepsin solution, as given above, was employed instead of a solution freshly prepared from the inner membrane of a hog's stomach. The residue from the pepsin digestion, after being thoroughly washed, was digested for six hours in 100 cc. of Stutzer's[1] pancreas solution. The extracted residue was then allowed to dry and the nitrogen determined by the Kjeldahl method. By this method 93.57 per cent. of total albuminoids were digested, only a slight increase over the amount digested by the pepsin solution alone.

3. *Stutzer's Method, Modified by Wilson.*[2]—The pepsin solution here employed was the same as in the preceding experiments. The pancreas solution was made by dissolving one and one-half grams of Merck's "absolute pure" pancreatin, and three grams of sodium carbonate in one liter of water. The well-washed residue from the pepsin digestion was digested for twelve hours in 100 cc. of this solution, with frequent stirring, a temperature of 40° being maintained in the water-bath in which the flasks were immersed. The residue was then filtered, washed, and the nitrogen determined by the Kjeldahl method.

By this method 93.21 per cent. of the total albuminoids were digested.

4. *Niebling's Method.*[3]—Two grams of the sample were washed with ether and introduced into a flask with 100 cc. of two-tenths per cent. hydrochloric acid. The contents of the flask were then heated to boiling and kept at that temperature for fifteen minutes, after which they were allowed to cool and were neutralized, or rendered very slightly alkaline with a solution of sodium carbonate. One hundred cc. of Stutzer's pancreas solution were then added (without previous filtration), and the flasks immersed in the water-bath, which was kept at the temperature of 37°–40° for six hours. The residues were then washed, dried, and kjeldahled.

[1] To prepare this solution take one kilogram of steer's pancreas which has been freed from fat as far as possible, pass through a sausage grinder, rub up in a mortar with sand and allow to stand exposed to the air twenty-four to thirty-six hours. Then add three liters of lime water, one liter of glycerol, sp. gr. 1.23, a little chloroform, and let stand from four to six days. Press through a bag and filter through filter paper. Before using, take 250 cc., add 750 cc. water containing five grams anhydrous sodium carbonate, heat to 37° to 40° for two hours and filter. *Landw. Versuchs-Stat.*, *1889*, 36, 321–328. See also U. S. Department of Agriculture, Chem. Div., *Bull.*, 13, part 8, 1028.

[2] *J. Soc. Chem. Ind.*, 10, 118; through Report Maryland Experiment Station, *1891*, 338.

[3] *Landw. Jahrb.*, *1890*, 19, 149–187.

The result showed that 93.28 per cent. of the total albuminoids were digested by this method.

5. *Niebling's Method, Modified.*—This method is the same as the one preceding except that the pancreatin solution given under Wilson's modification of Stutzer's method was used instead of Stutzer's pancreas solution. The sample was digested in the pancreatin solution for twelve hours. By this method, 93.21 per cent. of the albuminoids were digested.

It will thus be seen that closely agreeing results were obtained by the different methods of digestion with bread which was as free as possible from substances which might interfere with its digestion. It was next undertaken to ascertain the effect of alum on the same methods of digestion.

II. Digestion of Alumed Bread.

For this purpose two loaves of "alumed" bread were baked. The alum, in a fine powdered state, was thoroughly mixed with the flour before the dough was made. No. 1 contained eight-tenths gram, and No. 2, 428 grams crystallized alum in the two-pound loaf. As soon as baked the bread was dried, ground, and bottled as before. Loaf No. 1 contained 11.88 per cent., and No. 2, 12.06 per cent. albuminoids in the dried sample.

1. *Digestion in Pepsin Solution.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	89.11
2	4.28	80.98

From these figures it is evident that the digestion of albuminoids in a pepsin solution is greatly lessened by the presence of alum. This it is true is universally admitted, and the results of this method are merely given as confirmatory of the work of others.

2. *Stutzer's Method.*—By Stutzer's method, using, however, an artificial pepsin solution instead of the one used by Stutzer, the following results were obtained. Since all the alum would be removed by washing after the pepsin digestion in this method and the next, the amount of alum originally present was dissolved in a little water and added to the sample previous to the pancreatic digestion.

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.56
2	4.28	92.40

It will be seen that these results would lead us to a conclusion entirely different, and almost contradictory, to the one which we would obtain from the results of the pepsin solution alone. Before making further comment, however, let us examine the results obtained by the other methods of digestion.

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.21
2	4.28	92.44

4. *Niebling's Method.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.54

5. *Niebling's Method, Modified.*—

No.	Grams alum.	Per cent. digestible albuminoids.
1	0.8	92.74
2	4.28	92.02

It is evident from these results that the custom of judging the influence of alum on the digestion by its effect on the digestion in the pepsin solution alone has led to grave errors. It is evident that the presence of alum interferes materially with the gastric digestion, but the aluminum seems to be precipitated by the alkali of the pancreatic fluid, so that a portion of the digestion which should be effected by the former ferment is effected by the latter. Of course, this paper does not take into consideration the toxic properties of alum, but we are led to believe that its influence on the digestion has been greatly overestimated.

III. Digestion of Bread Containing Aluminum Hydroxide.

It was next desired to ascertain the digestibility of bread which contained aluminum hydroxide but was free from the soluble salts which result from the use of baking powders. For this purpose two two-pound loaves of bread were baked, ground, and dried as before. Loaf No. 1 contained 0.54 gram of aluminum hydroxide, corresponding to about 3.24 grams of crystallized

alum. This amount might readily be obtained by the use of an alum baking powder. Loaf No. 2 contained two and one-half grams of aluminum hydroxide, a larger amount than should ever be found in bread.

This aluminum hydroxide was prepared by precipitation from an alum solution by means of ammonium hydroxide and washing with hot water till all soluble salts were removed. It was then heated to 100° till perfectly dry, and finely powdered in a mortar. The dried and powdered aluminum hydroxide was thoroughly mixed with the flour before the dough was made.

1. *Digestion in Pepsin Solution.*—As before stated, the evidence concerning the solubility of aluminum hydroxide which has been heated to 100° in the gastric juice is of the most contradictory description. Portions of two grams each of these samples were treated with 100 cc. of the acid pepsin solution with the following results:

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	87.03
2	2.50	86.78

According to these results the presence of aluminum hydroxide interferes materially with the digestion of albuminoids in a pepsin solution. We notice, however, that this retarding influence is not by any means proportional to the amount of hydroxide present. Indeed, although widely differing quantities of hydroxide were taken, their effect seems to be approximately the same. It seems probable, therefore, that even a much smaller amount of aluminum hydroxide might have given approximately the same results as the amounts employed. Concerning this point Hehner[1] found that when only a small amount of aluminum hydroxide was present its detrimental influence on the pepsin digestion was equal to that of an equivalent amount of alum, but when a larger amount was taken its effect was relatively less.

2. *Stutzer's Method.*—As before, a solution of Merck's granulated pepsin was used in this method in place of Stutzer's pepsin solution. The following results were obtained:

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	92.18
2	2.50	90.43

[1] *Analyst*, *1893*, 18, 213.

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	92.00
2	2.50	90.21

4. *Niebling's Method.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	91.77
2	2.50	89.13

5. *Niebling's Method, Modified.*—

No.	Grams aluminum hydroxide.	Per cent. digestible albuminoids.
1	0.54	91.90
2	2.50	88.96

Methods 4 and 5 give results which are noticeably lower than were obtained by the other methods. Their lack of agreement with each other also is such as to cause a serious error if these methods were adopted for this work.

These results make it evident that with aluminum hydroxide, as with alum, the results by the pepsin digestion alone cannot be taken as a guide to the influence of the aluminum hydroxide resulting from the use of an alum baking powder on the digestion. Here, as with alum, the albuminoids whose digestion is prevented in the pepsin solution by dissolved aluminum compounds, seem to be almost all digested by the alkaline pancreas solution. It is true that the digestion is not quite as complete in the presence of alum or aluminum hydroxide as in their absence. It is possible that this is due to the presence of sodium aluminate in the pancreas solution.[1] Although it appears that the influence exerted on the digestion of albuminoids by aluminum hydroxide is very slight, the possible toxic effects of even the slight amount of aluminum chloride produced in the gastric juice should not be overlooked.

IV. Digestion of Bread Containing Aluminum Phosphate.

It seems to have been quite generally assumed that aluminum phosphate was much less soluble in the gastric juice than aluminum hydroxide, and that it would exert a correspondingly less influence on digestion. Indeed, some have gone so far as to

[1] See Dunstan, *Analyst*, *1893*, 18, 152.

state that the only influence which could be exerted by the compounds resulting from an aluminum phosphate baking powder must be due to the soluble salts. In order to determine the effect of aluminum phosphate in the absence of the soluble salts, the preceding set of digestions was repeated with bread containing aluminum phosphate. Two two-pound loaves of bread were baked with the addition of aluminum phosphate and prepared for analysis as before. Loaf No. 1 contained 0.64 gram of aluminum phosphate, which is equivalent to 2.56 grams of crystallized alum. This amount has frequently been found in bread prepared by alum baking powder. Loaf No. 2 contained 3.20 grams of aluminum phosphate, an amount largely in excess of that usually found in bread.

For the preparation of this compound, alum was dissolved in water, an excess of hydrogen disodium phosphate added, and the resulting precipitate washed with water until the filtrate ceased to be acid. It was then dried at 100° and reduced to a fine powder in a mortar. The dried and powdered aluminum phosphate was thoroughly mixed with the flour before the dough was made.

1. *Digestion of Pepsin Solution.*—Portions of the samples were digested in the acid pepsin solution, as before, after washing with ether to remove the fat. The following results were obtained:

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	80.87
2	3.20	71.21

Comparing the result obtained in sample 1 with that obtained by the peptic digestion of alumed bread, we find that even when a relatively large amount of aluminum phosphate is present, its effect on the pepsin digestion is equal to that of an equivalent amount of alum. It is also apparent that its effect is much greater than that of an equivalent amount of hydroxide.

2. *Stutzer's Method.*—As in the previous digestions, this method was modified by substituting a solution of Merck's granulated pepsin for Stutzer's pepsin solution. The following results were obtained:

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	83.11
2	3.20	78.26

3. *Stutzer's Method, Modified by Wilson.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	82.56
2	3.20	81.32

4. *Niebling's Method.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	86.35
2	3.20	82.18

These results differ materially from those obtained by the other methods of digestion.

5. *Niebling's Method, Modified.*—

No.	Grams aluminum phosphate.	Per cent. digestible albuminoids.
1	0.64	86.46
2	3.20	81.74

These results agree fairly closely with those obtained by method 4, but are materially lower than those obtained by methods 2 and 3.

From these results it appears that the influence of aluminum hydroxide on the digestibility of bread is about the same as that of an equivalent amount of alum, when present in about the quantity which is usually found as a result of the use of alum baking powder which contains no phosphate.

The action of aluminum phosphate is quite different, however, for notwithstanding the supposed insolubility of this compound, ten to twelve per cent. of the albuminoids which are digestible in the presence of alum or aluminum hydroxide appear to be insoluble in the presence of an equivalent amount of the phosphate.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY.—No. 9.]

SOME CHARACTERISTICS OF CALIFORNIA WINES.

BY W. H. KRUG.

AMONG the exhibits of American products at the World's Columbian Exposition, at Chicago, in the year 1893, one of the most interesting and varied was that of the California wine producers at the California State Building. The wines shown there, represented all the important districts in the state and the various types grown. At the suggestion of Dr. H. W. Wiley, Chief Chemist of the U. S. Department of Agriculture, the Cali-

fornia viticultural commission sent a set of these wines to the laboratory of the department, where they were analyzed under my supervision. All important varieties were represented and the analyses were made as complete as possible. The wines were classified as follows:

DRY WHITE WINES—	36 of the Rhenish type.
	38 of the Sauterne type.
	6 of the white Burgundy type.
	7 miscellaneous.
DRY RED WINES—	37 of the Claret type.
	22 of the Medoc type.
	20 of the Burgundy type.
SWEET OR FORTIFIED WINES—	6 of the Sherry type.
	13 of the Port type.
	9 miscellaneous.
	—In toto, 194.

GENERAL REMARKS.

California wine producers grow European types almost exclusively, and it will be seen from the table of analyses that they aim to follow these types in their description as closely as possible. This is carried even to the extent of adopting the various styles of bottles used in the European trade.

A few of the white wines were considerably deeper in color than the European wines of the same type. By far the greater number, however, were perfectly clear and brilliant, showing that great care had been exercised in maturing and preparing for bottling. This was especially true of the red wines. The following determinations were made:

Specific gravity, alcohol by weight, alcohol by volume, extract, total acidity as tartaric acid, polarization of 26.048 grams in a 200 mm. tube, polarization of the wine in a 220 mm. tube, Wild polariscope, reducing sugar as dextrose, glycerol, tannin and coloring matter, albuminoids, ash, sulphuric acid in ash, potassium sulphate in 100 cc. of wine stated in grams, chlorine in ash, sodium chloride in 100 cc. of wine stated in grams, insoluble residue in ash, sulphurous acid and salicylic acid.

In the sweet wines, the polarization was determined after inversion and after fermentation, the result being stated both in terms of 26.048 grams and of the original sample. The work on the

color intensity, and the presence of foreign coloring matters, has been delayed unavoidably and will not be ready in time for incorporation in this paper. It is intended to make this branch of the investigation especially complete.

METHODS OF ANALYSIS.

Specific Gravity.—The specific gravity was taken on an analytical balance by means of a Westphal bob whose displacement had been previously determined.

Alcohol.—One hundred cc. of the wine were placed in a flask with fifty cc. of water and a little precipitated calcium carbonate, the flask attached to an upright condenser and the contents of the flask subjected to distillation. To prevent the volatilization of the alcohol, the condenser tube should be made to extend almost to the bottom of the receiver. A 100 cc. flask was used for a receiver, and when 100 cc. of the distillate had passed over, the operation was interrupted and the flask removed, shaken, and the specific gravity of the distillate determined in the same manner as given under specific gravity. The percentage of alcohol by volume was determined from the specific gravity by table II, on page 213, in Bulletin 38, Division of Chemistry, U. S. Department of Agriculture, and the percentage of alcohol by weight was determined by multiplying the percentage of alcohol by volume, by the specific gravity of absolute alcohol and dividing that product by the specific gravity of the wine.

Extract.—The direct method was used. In the case of dry wines, fifty cc. were weighed and evaporated on the water-bath to a sirupy consistence in a platinum dish about eighty-five mm. in diameter. The residue was dried two and one-half hours in a drying oven at 100°. Of the sweet wines only ten cc. were weighed and diluted with distilled water before being evaporated.

Total Acidity (expressed as tartaric acid).—Ten cc. of the wine were carefully measured into a beaker, diluted with distilled water, and a few drops of neutral litmus solution added. Decinormal sodium hydroxide solution was used in the titration, and the neutral point was determined by placing a drop of the liquid on delicate litmus paper. This was found to work equally well on white and red wines. A standard solution of calcium hydrox-

ide has been recommended for red wines, the end reaction being the appearance of a flocculent precipitate. I found it much more difficult, however, to observe this than to note the neutral point with sensitive litmus paper. Before this point is reached the natural coloring matter of the wine will change, indicating the approach of neutrality so that the operator can work without difficulty to within a tenth of a cubic centimeter.

Glycerol.—A. In dry wines. One hundred cc. of wine were evaporated down to about ten cc. on the water-bath with about five grams of fine sand. Milk of lime was then added until the reaction was strongly alkaline, and the evaporation carried almost to dryness. The residue was gently heated on the water-bath with about fifty cc. of ninety-six per cent. alcohol, and mixed with a glass pestle until a homogeneous paste was obtained. It was allowed to settle and the supernatant liquid filtered through a folded filter. The residue was repeatedly extracted in this manner until about 150 cc. of filtrate were obtained. To this a few pieces of glass or sand were added to prevent bumping, and the alcohol carefully distilled off over a small flame until about fifteen cc. remained. The evaporation was then continued on the steam-bath until the residue became sirupy. After cooling, it was dissolved in ten cc. of absolute alcohol and fifteen cc. anhydrous ether added, the flask well-stoppered and shaken. When the precipitate had collected on the sides of the flask, the clear liquid was decanted into a tared glass-stoppered weighing bottle capable of holding about fifty cc., the precipitate washed once or twice with a few cc. of a mixture of two parts of alcohol and three of ether, the washing being transferred to the weighing bottle. The ether-alcohol removed on the water-bath, the residue dried one hour in a water-oven and weighed. When the precipitate, caused by the addition of the ether, remains flocculent, it is separated by filtering through a small filter, which is then washed repeatedly with a few cc. of the ether-alcohol mixture.

B. In sweet wines. One hundred cc. of the wine are evaporated to a thick sirup on the water-bath with about ten grams of sand. The residue is repeatedly extracted with absolute alcohol until from 100 to 150 cc. have been used (the amount being

varied with the amount of sugar present). The extracts are united in a large flask and one and one-half parts ether added for every part of alcohol used. The flask is stoppered and allowed to stand until the liquid is clear. Almost all the sugar is present in the sirupy precipitate while the glycerol remains in solution. The clear liquid is decanted into a flask, the residue washed repeatedly with small quantities of the ether-alcohol mixture and the united liquids distilled. The evaporation is completed on the water-bath, the residue washed into a porcelain dish by means of a little water, and treated as in A.

Polarization.—The wines were all polarized in a Schmidt and Haensch instrument with a 200 mm. tube. In the case of the dry wines, fifty cc. were evaporated sufficiently to permit the addition of three cc. of lead subacetate solution and three cc. of a saturated sodium carbonate solution to the white, and respectively six cc. of each solution to the red wines. The precipitate was filtered off and the filtrate polarized. In the case of the sweet wines twenty-five cc. were taken and made up to fifty cc.

The sweet wines were both inverted and fermented. For inversion twenty-five cc. were placed in a fifty to fifty-five cc. flask, two and one-half cc. strong hydrochloric acid added. The flask was heated in a water-bath to 68° C., consuming about ten minutes in heating. It was removed, cooled quickly to room temperature, filtered, and polarized. For fermentation, fifty cc. were placed in a wide-mouthed flask, a quarter of a cake of Fleischmann's compressed yeast and a sufficient amount of a potassium fluorid solution added, so that ten mgms. of this salt were present. The flask was allowed to stand four days at room temperature when it was found that fermentation was complete. The liquid was then washed into a 100 cc. flask, four cc. of lead subacetate solution, two cc. of mercuric nitrate solution (U. S. Department of Agriculture, Division of Chemistry, Bulletin 38, p. 198), and a varying amount of thick alumina cream added. It was then made up to 100 cc. with water, filtered, and polarized. The mercuric nitrate solution was added to destroy any bacteria which might impair the transparency of the filtrate when the latter, by any chance, stood for a length of time before being polarized.

If, after inversion, the wine polarizes more strongly to the left, unfermented cane sugar is present.

If, after fermentation, it polarizes to the right, the unfermentable constituents of commercial glucose are probably present.

Reducing Sugar.—This was determined by Allihn's gravimetric method and was calculated as dextrose.

Reagents.—1. 34.639 grams of crystalline copper sulphate dissolved in water and diluted to 500 cc.

2. One hundred and seventy-five grams of Rochelle salt.

One hundred and twenty-five grams of potassium hydroxide.

Dissolved in water and diluted to 500 cc.

In white wines. Fifty cc. were neutralized with sodium carbonate, the alcohol removed by heating on the steam-bath, made up to the original volume with water and filtered through a dry filter. When necessary, this solution was diluted with water to bring the reducing sugar down to one per cent. or less.

Thirty cc. of the copper solution, thirty cc. of the seignette solution, and sixty cc. of water, were placed in a beaker and heated to boiling. Twenty-five cc. of the sugar solution were then added and the whole boiled two minutes. The cuprous oxide was immediately filtered off and washed with hot water. It was then dissolved in dilute nitric acid, reduced to copper by the usual electrolytic method and weighed in that form.

The red wines were decolorized by filtering through bone-black, the first portion being rejected and the second portion treated precisely as the white wines.

Tannin and Coloring Matter.—The Löwenthal method was used.

Reagents.—Permanganate of potash solution: 1.333 grams of crystallized potassium permanganate in a liter of water.

Indigo solution: Six grams of sodium indigo sulphate and fifty cc. concentrated sulphuric acid per liter of water.

Decinormal oxalic acid solution.

Washed bone-black suspended in water so as to make a thin paste.

A. One hundred cc. of wine were dealcoholized by boiling and the lost weight restored with water. Ten cc. of the dealcoholized wine are transferred to a large porcelain casserole, twenty

cc. of the indigo solution and about 750 cc. of distilled water added, and the titration carried out with the permanganate solution, adding a cubic centimeter at a time until the liquid becomes green, when it is added drop by drop until the color turns to golden-yellow. Result A.

B. Ten cc. of the dealcoholized wine are diluted with water, a few cc. of the bone-black added, the liquid well stirred with a glass rod and allowed to stand some time. The bone-black is then filtered off and washed repeatedly with water. The filtrate is diluted to about 750 cc. and titrated as in A after adding the indigo solution. Result B.

Result A—Result B=cubic centimeters required by the tannin and coloring matter. This is stated in terms of oxalic acid.

Ash.—The residue from the extract determinations was carefully incinerated and weighed. In the sweet wines, the ash was determined by charring the extract and exhausting with hot water. The insoluble residue, consisting mostly of carbon, was collected on a filter, washed, dried, and burnt separately, the residue from the water extract was added to this and the whole heated to low redness until white.

Albuminoids.—The Kjeldahl method was used, the wine being previously evaporated to dryness in the digestion flasks. The amount used varied with the wines, it being necessary to use as little as ten cc. of some of the sweet wines on account of the tendency to foam when digested with sulphuric acid.

Sulphuric Acid and Chlorine in the Ash.—The ash was digested with hot water and a few drops of nitric acid and filtered into a fifty cc. flask. The residue was washed with hot water until the flask was full to the mark. It was cooled, made up and the sulphuric acid estimated in an aliquot portion in the usual manner. In another portion the chlorine was determined volumetrically with $\frac{N}{200}$ silver nitrate solution. They were respectively converted to grams potassium sulphate and sodium chloride in 100 cc. of wine.

Insoluble residue in Ash.—The filter and residue were ignited in a weighed platinum crucible and weighed.

Sulphurous Acid.—In the determination of sulphurous acid 100 cc. of the wine were diluted in a distilling flask with fifty

cc. of water, acidulated with five cc. of dilute sulphuric acid (H_2SO_4 one part, H_2O, three parts). The distillation was carried on in an atmosphere of carbon dioxide and the distillate received in a flask containing a measured quantity of decinormal iodine solution. The condenser tube should extend well below the surface of the iodine solution and in case a current of carbon dioxide be passed through the apparatus, the receiving flask should be closed with a mercury valve or attached to a U tube containing a portion of the iodine solution. In the progress of the work it was found more convenient to expel the atmosphere by the addition of a small quantity of sodium carbonate and in this case the guard-tube was found to be unnecessary. After about 100 cc. have distilled over, the excess of iodine is determined with decinormal sodium thiosulphate solution.

Salicylic Acid.—The following method was worked out by Mr. W. D. Bigelow who had charge of this branch of the investigation.

Seventy-five cc. of the wine are placed in a separatory funnel, acidified with five cc. of dilute sulphuric acid (H_2SO_4 one part, H_2O three parts) and extracted with a mixture of eight parts of sulphuric ether and one part of petroleum ether. The ether is washed once with water and then thoroughly shaken with about twenty-five cc. of water and six to eight drops of a five-tenths per cent. solution of ferric chloride. The aqueous layer contains most of the coloring matter in combination with the iron and is discarded. The ether is then washed with water, transferred to a porcelain dish, evaporated to dryness and the residue heated to the full temperature of the steam-bath for a few minutes. When the dish has become cool from four to five cc. of water are added, the insoluble matter filtered off after a few minutes and the filtrates tested for salicylic acid by the addition of three to four drops of a five-tenths per cent. solution of ferric chloride. By this method an excellent clarification may be obtained with white wines and with most red wines. Sometimes, however, with the latter, a second extraction is necessary

General Remarks Concerning the Methods of Judgment.

There being no law in this country which governs and regu-

lates the chemical composition of wines it was deemed advisable to apply some foreign standard. It is true that our wines grown under different climatic and soil conditions cannot be judged with absolute fairness by a standard based on the composition of European natural wines. Such application can only be of value as a means of comparison and was applied only in such sense.

The standards used were those adopted in the German Empire. On account of the lengthiness of the report made by the Royal Commission empowered to frame the regulations, I will only mention the more salient points relating to the constituents of wine. They are as follows:

Wines which have been prepared solely from pure grape juice contain only rarely less than one and one-half grams extract per 100 cc. If, therefore, a wine is found to contain less it must be rejected unless it can be proved that other wines of the same type and year exhibit the same peculiarity.

After deduction of the "fixed acid" the extract-rest in natural wines equals at least one and one-tenth grams per 100 cc., after deduction of the total acid at least one gram.

A wine in which the ash equals more than ten per cent. of the extract, should contain a correspondingly larger amount of extract than is usually assumed to be a minimum. In natural wines the ash and extract are very often found to be in the proportion of one to ten. A considerable variation from this ratio, however, does not justify the assumption that the wine is adulterated.

In accordance with experience the free tartaric acid does not amount to more than one-sixth of the "fixed acids."

The ratio between glycerol and alcohol can vary in natural wines from 7:100 to 14:100. Wines having a different ratio have had either alcohol or glycerol added to them.

As during the various manipulations which the wine undergoes, small amounts of alcohol (not more than one per cent. volume) may get into the wine, this must be considered in judging wines. The above limits and ratios are not always applicable to sweet wines.

For the individual inorganic constituents no reliable limits

can be given. The supposition that better wines always contain more phosphoric acid is without foundation.

Wines containing less than 0.14 gram ash per 100 cc. must be rejected unless it is shown that other natural wines of the same type and year show the same peculiarity.

Wines containing more than 0.05 gram NaCl in 100 cc. must be rejected.

Wines containing more than 0.092 gram of SO_3 per 100 cc. (corresponding to two grams of K_2SO_4 per liter) must be designated as having been treated with gypsum, *i. e.*, plastered.

Various circumstances or influences can make a wine ropy, dark, brown, turbid, or bitter, or can change its color, taste, and odor. The coloring matter of red wines may thus be precipitated. None of the above phenomena justify the assumption that the wine is not genuine.

A second fermentation in a wine does not absolutely indicate the addition of sugar or sweet substances. Very often the original fermentation is hindered, or a sweet wine may have been added to the original completely fermented wine.

In only a few samples were deposits noticeable, most of the wines, both white and red, presenting a fine appearance and showing that they were well-matured before being bottled. Deposits were much more prevalent among the white than among the red wines. In the analytical tables, the wines are classified by types, and this classification is followed in the discussion as far as practicable.

To facilitate discussion of the results the most important points were arranged as follows:

1. Are substances present which are not characteristic of pure natural wines and deleterious to health?

2. Is the quantitative composition of the wines such as is shown by European natural wines?

3. In what manner have the manipulations varied from those used in the preparation of pure natural wines?

First.—Are substances present which are not characteristic of pure natural wines and deleterious to health?

Such substances may be unfermented cane sugar, the unfermentable constituents of glucose, potassium sulphate, sodium

chloride, sulphurous acid, and other preservatives. Some interesting data were obtained in this connection.

Among the twenty-eight sweet wines there was only one, Port, No. 12,814, that gave a zero polarization after fermentation. In every other instance, as will be seen from the tables, there was a dextro rotation showing possibly that commercial glucose had been used for purposes of fortification. It is well-known, however, that this substance is not used in California, and, therefore, this dextro rotation is not positive proof of the use of glucose. All but five gave an increased left-handed reading after inversion, indicating the presence of non-inverted sucrose. Although there can be no objection to the presence of sucrose or invert sugar, it has not been determined as yet whether the unfermentable constituents of glucose, the most important of which is amylin, exert any specific physiological action on the human body, and as long as this is the case any decision on their injuriousness must be withheld.

To produce sweet wines it is absolutely necessary to add some saccharine substance to obtain the desired strength in alcohol and requisite sweetness. It would be much more rational, however, for the producer to use cane sugar, which can be procured pure so easily, especially as it has hitherto been impossible to obtain pure dextrose at a price which would render its use profitable.

There were found only three wines which exceeded the German limit for potassium sulphate; namely, Gutedel, No. 12,678, with 2.321 grams per liter, Zinfandel, No. 12,713, with 2.392 grams per liter, and Burgundy, No. 12,714, with 2.315 grams per liter, the latter two being from the same winery. Plastering is therefore not used very much to excess by California wine producers. Plastering is the commercial term applied to the treatment of the grapes with burnt gypsum. All Spanish, Italian, and Greek wines are extensively plastered. In Greece, a layer of grapes is placed in a low cistern and well-covered with gypsum, which is followed with another layer of grapes in turn covered as before, this being continued until the cistern is full. After from twelve to twenty-four hours the grapes are mashed by treading and the must filled in casks. The use of gypsum

secures a quicker ripening and better color. The chemical changes taking place are, in brief, as follows:

The potassium bitartrate and calcium sulphate react forming calcium tartrate and potassium acid sulphate, of which the former, on account of its insolubility, separates almost entirely during fermentation. This insolubility is also the cause of the rapid clearing of the wine after fermentation. The improved color of a wine thus treated is stated by Kayser to be due to the presence of free phosphoric acid. Plastering has become very popular in France, as it enables the producers to supply a cheap red wine by avoiding the expense attached to a long period of ripening. Plastered wine contains the same amount of potash as the must, while in a natural wine the precipitation of potassium bitartrate decreases the potash more or less. Pure must contains rarely as much as two-tenths gram of SO_3 per liter, while in plastered wines this is greatly exceeded, often amounting to eight-tenths to two grams per liter. Plastered wines always show a higher ash than natural wines. Thus a wine of from eight to ten volume per cent. alcohol and 2.2–2.3 grams extract per 100 cc., which normally contains 0.2–0.25 gram of ash per 100 cc. will, after plastering, contain 0.28–0.35 gram. A plastered wine made from pure must will always contain at least one-tenth gram of potash per 100 cc., and usually considerably more.

From a physiological standpoint the only objection to plastered wines is the presence of potassium sulphate. Although it is evident that the consumption of a large quantity of such wines would be necessary to produce a physiological action on a normal individual, it must likewise be considered that much smaller quantities may be harmful to invalids and children. When we keep the fact in mind that the southern sweet wines are the ones preferred for medicinal use, and at the same time the ones most extensively plastered, we can appreciate the force of these remarks. None of the California sweet wines analyzed exceeded the limit, two grams per liter, although one, Port, No. 12,710, approached it with 1.861 grams per liter.

All the dry white and the sweet wines, with the exception of the Ports and Sherries, were examined quantitatively for sul-

phurous acid and only twelve were found that contained none. In every other case the amount present exceeded the limit placed by the German law. Even when we adopt the limit suggested by the Association of Bavarian Representatives of Applied Chemistry; namely, 0.01 gram per liter, we find that all the wines analyzed that were found to contain sulphurous acid exceed this by far. They are sulphured excessively. Sulphuring is, without doubt, one of the most important adjuncts to the manufacture of wine.

The use of sulphurous acid is very old. Arnolf de Villanova mentions it in his work on wine manufacture printed in 1830 and von Holburg in 1587 recommended the use of sulphur to fumigate the casks and directed to burn three sticks and then close the cask so as to retain the fumes. He found that this insured good and perfect wines that did not deteriorate on standing. In a book published in Nuremberg in 1708 entitled "Der Kuriose Kellermeister," the amount of sulphur required for a 600 liter cask is given as seventeen grams. In a book published in 1775 under the title "Treatise on the Improvement of Wine and the Prevention of Injurious Practices in Wine Making." This statement is made on page 75: "Fumigation is necessary and important, first to preserve the wines and cask and second to improve the wine."

Only twice have attempts been made to replace sulphur. Once when the use of alcohol was suggested and again when it was believed that an ideal preservative had been found in synthetic salicylic acid. Neither realized the expectations of its promoters and sulphuring to-day still holds the same position that it has for centuries. Sulphuring is used to fumigate the casks, to prevent oxidation in the wines, and to prevent diseases peculiar to the wines.

Technically the use of sulphur is, without doubt, wrong. Wine ages by a slow process of oxidation which is absolutely interrupted as long as any sulphurous acid is present. As a preservative, sulphurous acid in the amount used is not an unqualified success as is shown by the necessity of repeating sulphuring when a wine stands for some time before being consumed. Nessler found that from thirteen to eighty-one mgms.

per liter were required to prevent the browning and turbidity of red wines. Moritz found that the growth of mycoderma vini was not indefinitely hindered until 0.05 per cent. sulphurous acid was present. All these figures far exceed the limits of the European laws.

From a physiological standpoint the presence of sulphurous acid is objectionable not so much on account of any possible immediate action but more through the cumulative effect on the digestive tract. Such effects will rapidly become general throughout the whole nervous system. In connection with this the experiments of Braun and Bematzik are of interest. They are the only ones made on man and showed that doses of eighty mgms. upwards caused serious irritation of the alimentary canal. Husemann and Bischoff recorded several cases where the consumption of freshly sulphured wine caused physiological disturbances and severe headache in persons otherwise accustomed to wine.

A further objection is the formation of bisulphates and even of free sulphuric acid in frequently sulphured wine. These also have a physiological action which cannot well be overlooked.

Eighty-seven wines were examined for sulphurous acid. Thirty-three of those contained more than eighty mgms. sulphurous acid per liter. Of these twenty-nine contained over 100 mgms., nine of 200 mgms., and two over 300 mgms.

All wines were examined for salicylic acid and only four were found to contain this preservative; namely, Sauterne No. 12,631, heavy reaction; Claret No. 12,633, very heavy; Port No. 12,627, distinct; and Port No. 12,710, heavy. It is hardly necessary to explain the objections against this preservative and it is a pleasure to find it so little used by wine producers in California. Nos. 12,627, 12,631, and 12,633 are wines from the same firm.

Second.—Is the quantitative composition of the wines such as is shown by natural wines?

All the wines analyzed show when compared with European wines one striking difference, their much lower glycerol-alcohol ratio. According to the German law this should not be lower than seven nor higher than fourteen, sweet wines to be excepted. A glance at the analyses will show that in California wines it

rarely rises to eight or above and that the average is from five to six. Baumert in his work on seven California wines also found this to be the case and makes the assertion that it is due to a slight alcoholizing of the wines. In our work we have, however, found it to be a general characteristic and it hardly seems possible that wine producers should practice this mode of fortification so universally. I am rather inclined to believe that the proper solution of the problem will be found in a careful study of the processes of fermentation as they take place in the California wines. It is probable that the fermentation takes place too rapidly to permit of the formation of a proper quantity of glycerol.

A comparison between the composition of California wines and European wines of the same type is difficult as the propriety of applying the same form of judgment to two kinds of wine grown under different conditions of soil and climate is doubtful. Still it may be of interest to call attention to the points wherein they differ.

For purposes of comparison the analyses given in König, Chemie der menschlichen Nahrungs-und Genussmittel were used.

Wines of the Rhenish Type.—The California Riesling is distinguished according to these analyses by a higher alcohol and lower extract content, and a somewhat lower acidity. The percentage of glycerol present is in most cases much lower. The California Riesling varies from 8.45–11.67 per cent. alcohol by weight, 1.66–2.61 per cent. extract, 0.478–0.658 per cent. total acid as tartaric acid, and 0.501–0.932 per cent. glycerol, while German Riesling varies from 5.90–10.15 per cent. alcohol by weight, 1.7–3.21 per cent. extract, 0.395–1.250 per cent. total acid as tartaric acid, and 0.49–1.34 per cent. glycerol.

California Gutedel, on the other hand, is higher both in alcohol and extract, while the acidity is somewhat lower. It varies from 9.67–11.16 per cent. alcohol by weight, 1.67–2.34 per cent. extract, and 0.467–0.662 per cent. total acidity. German Gutedel shows from 7.12–8.23 per cent. alcohol by weight, 1.67–2.01 per cent. extract and 0.241–0.830 total acidity. The California wine shows in accordance with its higher percentage of extract a higher ash than the German wine.

No analyses of German Hock could be found, so it is impossible to draw comparisons on this wine, though its close agreement with the two wines just discussed makes it highly probable that it will exhibit the same characteristics. In general, these wines are all somewhat stronger in alcohol and higher in extract than the German wines of the same type.

Wines of the Sauterne Type.—A comparison of the minima and maxima and means of American Sauterne with those of French Sauterne show that although the average California Sauterne shows a higher alcohol content, wines are found on the French market that exceed the highest found in our work. California Sauterne shows a lower extract and acidity, while the percentage of glycerol is far below that found in French wines. The following figures will exibit this. California Sauterne: Alcohol by weight, 8.43–12.18 per cent., extract, 1.7–4.03 per cent., acidity, 0.422–0.641 per cent., and glycerol, 0.178–0.850 per cent. French Sauterne: Alcohol by weight, 9.05–12.49 per cent., extract, 2.47–3.54 per cent., acidity, 0.54–0.75 per cent., and glycerol, 0.866–1.03 per cent.

The same general characteristics are true of the other miscellaneous California white wines analyzed. On the whole, all these wines exhibit a higher alcohol, somewhat lower extract and acidity, and a much lower percentage of glycerol.

Wines of the Claret Type.—The various California representatives of the Claret type, the most important of which is the Zinfandel, all show a higher percentage of alcohol, extract and total acid, and a lower glycerol content than the French Clarets. California Zinfandel shows the following minima and maxima: Alcohol by weight, 9.15–10.5 per cent., extract, 2.28–3.37 per cent., total acidity, 0.635–0.871 per cent., glycerol, 0.446–0.634 per cent. California Claret gives the following figures: Alcohol by weight, 9.16–11.23 per cent., extract, 2.36–3.34 per cent., total acidity, 0.601–0.783 per cent., and glycerol, 0.484–0.620 per cent. French Clarets vary within the following limits: Alcohol by weight, 7.45–9.32 per cent., extract, 2.0–3.0 per cent., total acidity, 0.47–0.78 per cent., and glycerol, 0.55–0.99 per cent. In accordance with the higher extract a higher ash was found in California Clarets; *viz.*, 0.235–0.342 per cent., French Clarets giving 0.19–0.31 per cent.

Wines of the Medoc Type.—These wines are represented in California by the Cabernet, Malbec and Medoc. Only the last could be compared with French wines, no analyses of wines of the first two subtypes being found. Here it was again found that the California wines were characterized by a higher percentage in alcohol, extract and acidity, while the glycerol was much lower than in the French Medocs.

The following minima and maxima were obtained. California Medocs: Alcohol by weight, 11.75–12.4 per cent., extract, 2.33–2.92 per cent., acidity, 0.614–0.824 per cent., and glycerol, 0.371–0.556 per cent. French Medocs: Alcohol by weight, 9.50–10.70 per cent., extract, 1.96–2.60 per cent., total acidity, 0.380–0.680 per cent., and glycerol, 0.640–1.04 per cent. Corresponding to the higher extract a higher ash was found in the domestic wines; *viz.*, 0.304–0.386 per cent. French Medocs showing from 0.21–0.297 per cent.

Wines of the Burgundy Type.—Only one analysis of a Burgundy wine was in König. A comparison with this showed the California Burgundies to contain a higher percentage of alcohol, extract, acidity, and ash than French Burgundy, while the glycerol is lower. The following minima, maxima, and means were obtained:

CALIFORNIA BURGUNDY.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by volume	10.97	15.48	12.57
Extract	2.20	3.48	2.79
Acidity	0.594	0.783	0.674
Ash	0.190	0.362	0.283
Glycerol	0.464	0.640	0.551

CALIFORNIA MATARO.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by volume	9.58	13.40	12.38
Extract	2.24	3.39	2.79
Acidity	0.601	0.837	0.673
Ash	0.203	0.322	0.278
Glycerol	0.544	0.583	0.553

French Burgundy: Alcohol by volume, 11.23 per cent., extract, 2.63 per cent., acidity, 0.390 per cent., ash, 0.210 per cent., and glycerol, 0.680 per cent.

A general comparison of all California dry wines shows, therefore, that they are characterized by a high percentage of alcohol and low percentage of glycerol. In the white wines, the extract, acidity and ash are generally lower than in foreign wines while in the red wines these constituents are higher.

Sweet Wines.

Wines of the Sherry Type.—California Sherries on the whole are lower in alcohol than Spanish Sherries. They are higher in extract, which is due to the presence of unfermented grape sugar. The total acidity is higher while the ash and glycerol are lower. Following are the minima and maxima: California Sherry: Alcohol by weight, 14.38-17.57 per cent., extract, 3.33–9.38 per cent., acidity, 0.378–0.797 per cent., reducing sugar, 1.20–6.17 per cent., ash, 0.211–0.420 per cent., and glycerol, 0.325–0.722 per cent. Spanish Sherries: Alcohol by weight, 16.01–19.88 per cent., extract, 2.69–5.40 per cent., acidity, 0.250–0.640 per cent., reducing sugar, 0.52–3.77 per cent., ash, 0.200–0.660 per cent., glycerol, 0.220–0.910 per cent.

Wines of the Port Type.—These wines exhibit in general the same characteristics in comparison with Portuguese Ports as the Sherries; namely, a slightly lower percentage of alcohol, and a higher extract and acidity. The glycerol is in these wines slightly higher. The high extract is due to the presence of unfermented grape sugar. The following data were obtained: California Ports: Alcohol by weight, 11.97–17.40 per cent., extract, 8.52–16.51 per cent., acidity, 0.412–0.674 per cent., reducing sugar, 5.16–13.00 per cent., and glycerol, 0.161–0.688 per cent. Portuguese Ports: Alcohol by weight, 15.71–17.87 per cent., extract, 6.69–9.90 per cent., acidity, 0.290–0.470 per cent., reducing sugar, 4.42–8.12 per cent., and glycerol, 0.230–0.710 per cent.

Comparison of California Muscatel with Other Wines of that Name.

California Muscatel approaches the Syrian Muscatels in its alcohol content. No strict comparisons can be drawn between it and Sicilian Muscatels as the latter vary within too wide limits. It is stronger in alcohol and has in general a lower extract than the Greek Muscatels, due no doubt to the fact that

a large quantity of concentrated must is added to the finished wine in Greece so as to obtain a very sweet product. The glycerol content is higher and the ash and total acidity lower than in foreign Muscatels.

The following minima and maxima will show the differences existing:

CALIFORNIA MUSCATEL.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by weight	10.45	15.50	13.63
Extract	17.01	18.62	17.55
Acidity	0.317	0.405	0.369
Reducing sugar	43.18	16.30	14.66
Glycerol	0.866	1.014	0.941
Ash	0.148	0.192	0.113

SYRIAN MUSCATELS.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by weight	10.67	15.26	13.63
Extract	4.22	18.86	9.76
Acidity	0.430	0.830	0.646
Reducing sugar	0.25	4.50	3.13
Glycerol	0.320	2.00	0.857
Ash	0.210	0.960	0.495

GREEK MUSCATELS.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by weight	9.44	11.62	10.57
Extract	13.32	24.13	15.27
Acidity	0.410	0.751	0.566
Reducing sugar	13.50	18.86	15.01
Glycerol	0.564	0.950	0.718
Ash	0.290	0.388	0.321

SICILIAN MUSCATELS.

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Alcohol by volume	6.00	24.66	15.34
Extract	3.56	38.18	20.08
Acidity	0.270	1.140	0.630
Reducing sugar	12.50	29.01	17.16
Glycerol			
Ash	0.170	0.860	0.410

Five other samples of sweet wines were analyzed; namely, three Angelicas, one Tokay, and one Catawba. Of these, the Tokay is the most interesting as it differs in every respect from

the Hungarian Tokays. The percentages of alcohol and glycerol present are much higher; the extract, reducing sugar, acidity, and ash, lower. It is a more completely fermented wine.

Third.—In what manner have the manipulations differed from those employed to produce a pure natural wine?

With the exception of the extensive use of sulphur very little can be said against the dry wines. They are almost all well fermented and matured grape juice. All the white wines but twelve have been excessively sulphured, three exceeded the limit for potassium sulphate, and four contained salicylic acid.

Two wines of the Sauterne type, Nos. 12,653 and 12,775, were excluded from the averages as evidently not representative wines, No. 12,653 gave 6.69 per cent. extract, and 3.52 per cent. reducing sugar, while No. 12,775 gave 5.48 per cent. extract. The glycerol was respectively 0.432 and 0.456 per cent. They were evidently incompletely fermented wines.

No. 12,792, a dry white wine, proved an interesting sample. It furnished the following figures: Alcohol by weight, 9.53 per cent., extract, 1.1 per cent., glycerol, 0.321 per cent., ash, 0.191 per cent., ash extract ratio, 17.36 per cent., extract-rest, 0.56 per cent. There is no doubt in my mind that this is merely an artistic mixture that never saw a vineyard but had its birth in the cellar of some wine mixer.

Another sample, No. 12,684, a miscellaneous red wine, gave only 0.105 per cent. total acid. The manufacturer here, no doubt, has used chaptalization to reduce the acidity and succeeded beyond his expectation.

Cane sugar is undoubtedly used by many to sweeten their wines, as is shown by the increased laevo rotation after inversion.

On the whole, it is evident that the California dry wines are fully equal to the European wines, and the red wines are in every respect superior to the young French Clarets. The sweet wines are to be unconditionally preferred to the European southern wines containing the same amount of alcohol and extract, and not being plastered. Their superiority is already being appreciated in Europe, and it is only a question of time when an extensive foreign market will be open to this, one of our most promising home products.

The Influence of Commercial Glucose on the Polarization After Fermentation.

To determine this point, a number of fermentations were made with mixtures of solutions of sucrose and glucose of varying strength, the same method being used as was employed in the analytical work. The results were not as uniform as desirable, probably on account of unequal rate of fermentation. They showed, however, that the amount of sucrose which is apt to be present in a wine is completely fermented in two days, so that any dextro rotation observed after that time must be due to the presence of glucose or its non-fermentable constituents.

Table of Results of Experiments Made to Determine the Effect Commercial Glucose has on the Polarization after Fermentation.

Original polarization of sucrose.	Original polarization of glucose.	Polarization after two days.	Polarization after four days.
+37 80		0	0
+18.90		0	0
+ 9.45		0	0
.....	+16.33	+4.5	+5.0
.....	+16.33	+4.8	+3.8
.....	+ 9.80	+2.0	+1.8
.....	+ 9.80	+2.5	+1.8
.....	+ 3.27	+0.4	0
.....	+ 3.27	+1.0	0
+19.23	+16.33	+4.6	+2.8
+19.23	+16.33	+3.5	+3.3
+11.54	+16.33	+3.5	+2.3
+11.54	+16.33	+3.0	+2.3
+ 3.85	+16.33	+3.7	+2.4
+ 3.85	+16.33	+3.6	+3.9
+19.23	+ 9.80	+2.0	+1.7
+19.23	+ 9.80	+2.8	+2.1
+19.23	+ 3.27	+0.7	+0.9
+19.23	+ 3.27	+0.7	+0.5
+11.54	+ 9.80	+2.4	+1.0
+11.54	+ 9.80	+2.3	+1.0
+ 3.85	+ 9.80	+0.9	+0.3
+ 3.85	+ 9.80	+0.8	+0.3

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY.—No. 10.]

CONTRACTION OF AQUEOUS SOLUTIONS OF ACETONE.

BY K. T. P. MC ELROY.

IN the following determinations, mixtures of known weights of acetone and water were made, the specific gravity determined by a piknometer and from this figure the volume calculated. The acetone used was bought from a New York firm and was of good purity, being free from methyl alcohol. It was fractionated and the fraction retained was boiled over calcium chlorid under a reflux condenser for three days. This portion was once more fractionated. The portion finally used boiled at 56.4° (air). Other samples were prepared for comparison by distilling acetates and by purifying the New York article by means of the sulphite compound. These various preparations possessed essentially the same boiling points and specific gravity.

In detail the method employed was to weigh a flask, add water, weigh, add acetone, reweigh, mix the united fluids by shaking and finally determine the specific gravity, first at 20° and then without refilling the piknometer, at 25°. The figures thus obtained are given in the annexed table:

TABLE I.

Weight acetone. Grams.	Weight water. Grams.	Acetone. Per cent.	Water. Per cent.	Total weight. Grams.	Specific gravity 20°.	Specific gravity 25°.
39.7256	2.0878	95.01	4.99	41.8134	0.80717	0.80174
37.4627	4.1328	90.09	9.91	41.5955	0.82172	0.81626
33.4936	4.6211	87.88	12.12	38.1147	0.82784	0.82278
32.3374	8.0688	80.04	19.96	40.4062	0.84972	0.84443
30.1632	10.0480	75.02	24.98	40.2112	0.86342	0.85796
28.1373	12.0375	70.04	29.96	40.1748	0.87495	0.87051
24.2140	16.1070	60.06	39.94	40.3210	0.89920	0.89469
20.1621	20.0854	50.10	49.90	40.2475	0.92078	0.91656
16.1438	24.1902	40.03	59.97	40.3360	0.94057	0.93695
12.5495	28.1583	30.83	69.17	40.7078	0.95606	0.95286
8.0333	32.8027	19.67	80.33	40.8360	0.97270	0.97024
4.0120	36.0740	10.01	89.99	40.0860	0.98507	0.98337

In table II these weights are recalculated into volumes at 20° and the per cent. of contraction for that temperature calculated. The figures representing the weights of the acetone were divided by the specific gravity of acetone at 20° (0.79197) and the volume

occupied at that temperature thus found. The same operation performed on the weight of the water, using the figure 0.99826, gave the volume of that liquid. These two volumes added together gave the figures recorded in the fifth column under "sum". The weight of the mixed acetone and water divided by the specific gravity at 20° gave the actual volume occupied by the mixture at that temperature. The difference between this figure and that representing the sum of the volumes of the unmixed liquids, when divided by the latter figure gave the "Per cent. of Contraction," the figure recorded in the last column.

TABLE II. VOLUME AT 20°.

Acetone. Per cent.	Water. Per cent.	Acetone. Cubic centimeter.	Water. Cubic centimeter.	Sum. Cubic centimeter.	Actual volume.	Contraction. Per cent.
95.01	4.99	50.161	2.091	52.252	51.802	0.861
90.09	9.91	47.303	4.140	51.443	50.620	1.600
87.88	12.12	42.291	4.629	46.920	46.041	1.873
80.04	19.96	40.831	8.083	48.914	47.552	2.784
75.02	24.98	38.086	10.065	48.151	46.572	3.279
70.04	29.96	35.528	12.058	47.586	45.919	3.503
60.06	39.94	30.574	16.135	46.709	44.840	4.002
50.10	49.90	25.458	20.120	45.578	43.710	4.089
40.03	59.97	20.384	24.232	44.616	42.885	3.880
30.83	69.17	15.845	28.207	44.052	42.579	3.344
19.67	80.33	10.143	32.860	43.003	41.982	2.374
10.01	89.99	5.066	36.137	41.203	40.694	1.236

The weights, recalculated in the same way but using the specific gravities of water and acetone at 25°, which are respectively 0.78630 and 0.99712, are recorded in the following table:

TABLE III. VOLUME AT 25°

Acetone. Per cent.	Water. Per cent.	Acetone. Cubic centimeter.	Water. Cubic centimeter.	Sum. Cubic centimeter.	Actual volume.	Contraction. Per cent.
95.01	4.99	50.522	2.094	52.616	52.153	0.880
90.09	9.91	47.644	4.144	51.788	50.958	1.603
87.88	12.12	42.596	4.634	47.230	46.324	1.918
80.04	19.96	41.126	8.092	49.210	47.850	2.779
75.02	24.98	38.361	10.077	48.430	46.858	3.241
70.04	29.96	35.784	12.072	47.856	46.151	3.561
60.06	39.94	30.795	16.153	46.948	45.067	4.006
50.10	49.90	25.642	20.143	45.785	43.911	4.093
40.03	59.97	20.531	24.260	44.791	43.050	3.889
30.83	69.17	15.960	28.240	44.200	42.722	3.344
19.67	80.33	10.217	32.897	43.114	42.090	2.374
10.01	89.99	5.102	36.180	41.282	40.764	1.255

Taking the figures in Tables II and III and calculating the contractions for every five per cent. by simple interpolation the following table is obtained:

TABLE IV.

Water.	Acetone.	Contraction at 20°.	Contraction at 25°.	Water.	Acetone.	Contraction at 20°.	Contraction at 25°.
0.00	100.00	0.000	0.000	49.90	50.10	4.089	4.093
4.99	95.01	0.861	0.880	50.00	50.00	4.087	4.091
5.00	95.00	0.863	0.882	55.00	45.00	3.983	3.987
9.91	90.09	1.600	1.603	59.97	40.03	3.880	3.889
10.00	90.00	1.611	1.616	60.00	40.00	3.876	3.887
12.12	87.88	1.873	1.918	65.00	35.00	3.589	3.632
15.00	85.00	2.208	2.234	69.17	30.83	3.334	3.334
19.96	80.04	2.784	2.779	70.00	30.00	3.272	3.272
20.00	80.00	2.789	2.783	75.00	25.00	2.838	2.837
24.98	75.02	3.279	3.241	80.00	20.00	2.403	2.403
25.00	75.00	3.280	3.242	80.33	19.67	2.374	2.374
29.96	70.04	3.503	3.561	85.00	15.00	1.824	1.833
30.00	70.00	3.505	3.563	89.99	10.01	1.236	1.255
35.00	65.00	3.753	3.787	90.00	10.00	1.235	1.254
39.94	60.06	4.002	4.006	95.00	5.00	0.619	0.627
40.00	60.00	4.003	4.007	100.00	0.00	0.000	0.000
45.00	55.00	4.046	4.050				

It was originally intended to make a determination for every five per cent. increase in the amount of acetone in the mixtures, but owing to an accident, a portion of the purified acetone was lost and from seventy per cent. acetone down, the determinations were made for each ten per cent. It will be noticed by an inspection of the table that the two series of figures, those for 20° and those for 25°, do not vary materially from each other, showing that between these temperatures the contractions of mixtures of the two liquids are practically the same. The contraction appears to reach its maximum where the weights of acetone and water employed are equal, but there is no great difference between a forty per cent. mixture and one with sixty.

ON THE HYDRATION OF CALCIUM BROMIDE AND IODIDE.[1]

BY CHARLES O. CURTMAN.

Received July 16, 1894.

THE official calcium bromide of the U. S. P. is intended to be substantially anhydrous, and to contain 99.7 per cent. of pure calcium bromide. Such a salt may be obtained by saturating a solution of hydrobromic acid with pure calcium carbonate, filtering, and evaporating the solution to dryness at a temperature considerably below a red heat (about 360° C.). A solid salt may at first be obtained, containing considerable water, which melts at about 80°–81° C., and in composition closely approximates the formula $CaBr_2 + 3H_2O$. This fused salt continues to lose a small amount of water, even a few degrees above that temperature, so that it is difficult to obtain a fused salt of a definite composition.

When the heat is raised to about 180°–181° C. a greater activity appears to take place in the separation of water, and if the fused mass be cooled at that point, a salt is obtained whose formula would somewhat approximate $2CaBr_2 + 5H_2O$. At a higher temperature the water separates with a kind of effervescence, leaving a spongy, anhydrous mass.

It appears to be probable that a hydration corresponding to $CaBr_2 + 3H_2O$ exists, and may be obtained by very careful fusion at 80° C., while the intermediate one, at about 180° C., may be a mere coincidence, though closely approached by two of the commercial specimens examined.

A similar behavior was observed with *calcium iodide*, made by saturation of hydriodic acid with calcium carbonate. The salt, which fuses below the temperature of boiling water, closely approaches the formula $CaI_2 + 3H_2O$, but cannot well be isolated by fusion, on account of a gradual loss of water, even below 100° C. With a rising temperature the water escapes very slowly and gradually, and towards the end with a slight effervescence, leaving a spongy, anhydrous mass. There was no

[1] Report of Research Committee B. No. 4.

appearance of any definite intermediate stage of hydration, as was observed with the bromide.

Six specimens of calcium bromide, manufactured by different firms, were obtained in the market. They all contain water, but by no means in uniform proportions, and but little calcium bromide can be found which conforms to the directions of the U. S. P. for anhydrous salt. The following is a short résumé of the analysis of the six specimens:

No. 1. (*M.*)—Dry white powder. When 1.9109 grams were heated for half an hour to 80° C., neither fusion nor loss of weight occurred. When heated till the preparation became spongy and anhydrous, it lost 0.3250 gram, corresponding to 17.007 per cent. of water, and 82.993 per cent. of calcium bromide. When titrated with silver nitrate and potassium chromate as indicator, it showed 82.98 per cent. of calcium bromide.

No. 2. (*M.* "*Dry.*")—Dry white powder. 1.032 grams were heated to 86° C. without loss of weight or fusion. When heated to perfect dryness the loss was 0.164 gram = 15.9 per cent. of water, and 84.1 per cent. of calcium bromide. Titration with silver nitrate yielded eighty-four per cent. of calcium bromide.

No. 3. (*M. C. W.*)—White granules, which melt between 80° and 81° C. When heated to 86° C. for half an hour one gram lost 0.0032 gram = 0.32 per cent. of moisture. When heated to perfect dryness, one gram lost 0.1816 gram = 18.16 per cent. of water and 81.84 per cent of calcium bromide. In titration with silver nitrate, 0.44 gram of the salt required 36.1 cc. of decinormal silver nitrate = 81.81 per cent. of calcium bromide.

This closely approaches the proportion of $2CaBr_2 + 5H_2O$, which requires 18.34 per cent. of water and 81.66 per cent. of calcium bromide.

No. 4. (*R.*)—White semi-fused lumps which melt between 80° and 81° C. When heated to dryness, 1.1036 grams lost 0.2349 gram, corresponding to 21.28 per cent. of water and 78.72 per cent. of dry substance. In titration, 0.2493 gram required 19.65 cc. of decinormal silver nitrate, corresponding to 78.6 per cent. of calcium bromide. The composition closely approaches the formula $CaBr_2 + 3H_2O$, requiring 21.27 per cent. of water.

No. 5. (*P.*)—White granules, melting below 100° C. 0.702

gram heated to dryness lost 0.1325 gram = 18.88 per cent. of water, and 81.12 per cent. of dry substance. Titration showed eighty-one per cent. of calcium bromide. (An approximation to the formula $2CaBr_2 + 5H_2O$, requiring 18.34 per cent. of water.)

No. 6. (*P. W.*)—White granules and semi-fused lumps. 1.32 grams heated to dryness lost 0.2323 gram = 17.6 per cent. of water, and 82.4 per cent. of dry substance. Titration showed eighty-two per cent. of calcium bromide.

A series of analyses of commercial specimens of calcium iodide gave similar results. The hydration in most cases made a close approach to the formula $CaI_2 + 3H_2O$, which requires 84.465 per cent. of calcium iodide, and 15.535 per cent. of water. No preparation came into my hands showing an intermediate hydration between three molecules of water and the anhydrous state.

The result of the examination is summarized as follows:

No 1. (*M. C. W.*)—White, fused lumps. Contain 84.29 per cent. of calcium iodide, and 15.71 per cent. of water.

No. 2. (*M.*)—Yellowish-brown granules. Contain 83.92 per cent. of calcium iodide, and 16.08 per cent. of water.

No. 3. (*R.*)—White fused mass. Contains 84.1 per cent. of calcium iodide, and 15.9 per cent. of water.

No. 4. (*P.*)—Yellowish-brown granules. Contain 85.37 per cent. of calcium iodide, and 14.63 per cent. of water.

No. 5. (*P. W.*)—White, fused lumps. Contain 84.3 per cent. of calcium iodide, and 15.7 per cent. of water.

Specimens 1, 3, and 5, show a trace of nitrate.

From the foregoing it is very probable that a definite hydrate of calcium iodide exists, having three molecules of water, for the deviations from such a formula in all of the commercial specimens examined are not very large.

To reach more conclusive evidence it would be necessary to obtain the salt in definite crystals. Hence, solutions of calcium bromide and calcium iodide were made in water saturated at a temperature of 80° C., also in alcohol of various degrees of dilution (for a high per cent. alcohol would most likely furnish an anhydrous product). The temperature of the atmosphere being high (30°–36° C.) artificial refrigeration had to be resorted to.

The result was rather disappointing. The alcoholic solutions remained clear for many hours. From the aqueous solutions crystals of both bromide and iodide were obtained, but of such small size that it was difficult to make out their forms. Those of the iodide were slightly larger and less deliquescent and under the microscope showed rhombic needles and prisms, somewhat rounded, so as to resemble some forms of uric acid.

But they were so difficult to separate from the solution without adhering liquid, that weighing could only be approximate, and most likely would include some liquid as well as the dry substance.

The bromide, on titration, yielded 62.3 per cent. of calcium bromide, which would approximate the formula $CaBr_2 + 6H_2O$, which requires 64.92 per cent. of calcium bromide, and 35.08 per cent. of water.

The iodide yielded 69.9 per cent. of calcium iodide; the formula $CaI_2 + 6H_2O$ would demand 73.11 per cent.

In both salts the adhering liquid would render the result somewhat uncertain, and the yield of dry substance too low.

The evidence thus far is certainly not sufficient to draw definite conclusions, but I believe that the existence of hydrates of the formula $CaBr_2 + 6H_2O$ and $CaBr_2 + 3H_2O$, as well as of the corresponding hydrates of calcium iodide, is very probable.

July 8, 1894.

A STUDY OF THE CHEMICAL BEHAVIOR OF ARSENOPYRITE.

By Thomas Montgomery Lightfoot.

Received June 23, 1894.

THE variation in the weathering of pyrite, marcasite, and pyrrhotite, so often to be observed in nature, has already furnished material for several papers on the subject. The consideration of these differences in behavior leads to the question involving the chemical difference between these and allied mineral species. The effect of the electric current on these naturally occurring sulphides and sulpharsenides has already been investigated in this laboratory, but, so far as I am aware, no series of experiments with various oxidants has been recorded. Investigations as to the effect of potassium permanganate on

pyrite,[1] marcasite,[1] and pyrrhotite have been in progress during the period occupied by the experiments described in this paper. At the suggestion, therefore, of Prof. Edgar F. Smith, I undertook the study of arsenopyrite in several directions with the results that follow.

The material used in this investigation was obtained from the dump of an abandoned mine in Maine and was purchased from a dealer. The mineral was associated with quartz, with apparently no other impurity so far as the mass was concerned. To separate this quartz the mass was crushed until it passed through a twenty-four mesh screen; it was then subjected to a rising stream of water in a ∪ tube which floated off the quartz and mixed grains. The material remaining in the tube was found to be entirely free from quartz. The pure material was then washed with distilled water, spread on a filter paper, and dried at a gentle heat. A magnet was used to remove any particles of iron that might have entered the material from the crusher. This purified arsenopyrite was then preserved in a glass-stoppered bottle, and portions of it ground from time to time as required in an agate mortar. An estimation of the total sulphur contained in this arsenopyrite gave as the average of three determinations 19.77 per cent., almost the theoretical for the ratio of FeS_2 to $FeAs_2$ as 1 : 1.

Action of Potassium Permanganate at the Ordinary Temperature.—The first series of experiments consisted in determining the effect of potassium permanganate solutions of varying strengths on the mineral, the oxidant being allowed to act for varying periods of time and at 100° as well as at the ordinary temperature (21°–22°). The method of procedure at the ordinary temperature was the same in each case, and was as follows: Two-tenths of a gram of the finely ground mineral were introduced into a glass-stoppered bottle and fifty cc. of the permanganate solution added. The bottle and its contents were then shaken at frequent intervals to prevent the caking of the mineral against the walls of the vessel and to expose fresh surfaces to the action of the permanganate. Four strengths of solution were employed, $\frac{1}{100}$ normal, one per cent., three per cent., and five

[1] See "A Comparative Study of the Chemical Behavior of Pyrite and Marcasite," by A. P. Brown. *Proc. Amer. Philos. Soc.*, 1894.

per cent., and each was allowed to act for periods of one, two, three, four, and five hours. Duplicate trials were made in each case. After the solution had been in contact with the mineral for the specified time the contents of the bottle were thrown on a filter, the residue was washed on the filter and rejected, and the filtrate was acidified with hydrochloric acid and the sulphur oxidized, and determined as barium sulphate. In this determination trouble was experienced in obtaining complete precipitation of the sulphuric acid, even after long digestion and standing, and this may account in part for the great irregularities shown in the results of these oxidations. It should be noted that the four-hour experiments (which show notable irregularities) were performed after the completion of the rest of the series, but presumably under the same conditions.

The results of this series of oxidations are tabulated below. It will be noticed that the two results given in each case sometimes correspond closely with each other and at other times one is more than double the other. There is no reason why these results should vary in this way so far as external conditions are concerned as these duplicates were in each case made at the same time and under the same conditions. The average of the two in a number of cases would seem to be nearer the expected result. Omitting consideration of the four-hour trials, reference to which has already been made, it is seen that in each case the oxidation is practically completed at the end of the first hour, and is comparatively slight after all. The mineral is not nearly so readily affected by this oxidant as the simple iron sulphides.

(1) TABLE SHOWING THE AMOUNT OF SULPHUR OXIDIZED IN ARSENOPYRITE BY POTASSIUM PERMANGANATE AT THE ORDINARY TEMPERATURE.

Strength of permanganate solution.	One hour. Sulphur oxidized. Per cent.	One hour. Average. Per cent.	Two hours. Sulphur oxidized. Per cent.	Two hours. Average. Per cent.	Three hours. Sulphur oxidized. Per cent.	Three hours. Average. Per cent.	Four hours. Sulphur oxidized. Per cent.	Four hours. Average. Per cent.	Five hours. Sulphur oxidized. Per cent.	Five hours. Average. Per cent.
$\frac{1}{100}$ normal..	0.34	0.33	0.34	0.34	0.33	0.41	0.53	0.52	0.52	0.36
	0.33		0.34		0.49		0.51		0.27	
1 per cent...	0.25	0.42	0.31	0.28	0.38	0.39	0.73	0.74	0.25	0.35
	0.58		0.24		0.40		0.75		0.46	
3 per cent...	0.61	0.56	0.43	0.36	0.40	0.39	1.20	1.30	0.55	0.50
	0.52		0.28		0.38		1.40		0.44	
5 per cent...	0.41	0.29	0.27	0.51	0.34	0.52	0.25	0.44	0.59	0.48
	0.16		0.75		0.69		0.63		0.33	

Action of Potassium Permanganate at 100°.—In conducting experiments at 100° the bottles containing the mineral and permanganate solution were suspended in boiling water, which covered about one-half of the bottle, and the stoppers introduced after the contents of the bottle had reached the temperature of the water. The other details of these experiments were the same as for those conducted at the ordinary temperature. The action in this case was considerably more energetic, and the results obtained were much more concordant. The best results in this case were with the $\frac{1}{100}$ normal solution which are remarkably close in duplicate and the averages show a regular rise in the amount of sulphur oxidized in proportion to the time of oxidation. The one per cent. solution gave discordant results, but curiously the averages show a fairly regular rate of oxidation. The three and five per cent. solutions give concordant results in duplicate and show on the other hand an approach to the character of oxidation shown at the ordinary temperature, but several times greater in degree. The oxidation for each of the three and five per cent. solutions seems to be nearly complete at the end of the first hour, the rate of oxidation thereafter being very slow.

The results of this series of experiments are given in the following table, along with their averages:

(2) TABLE SHOWING THE AMOUNT OF SULPHUR OXIDIZED IN ARSENOPYRITE BY POTASSIUM PERMANGANATE AT 100°

Strength of permanganate solution.	One hour. Sulphur oxidized. Per cent.	One hour. Average. Per cent.	Two hours. Sulphur oxidized. Per cent.	Two hours. Average. Per cent.	Three hours. Sulphur oxidized. Per cent.	Three hours. Average. Per cent.	Four hours. Sulphur oxidized. Per cent.	Four hours. Average. Per cent.	Five hours. Sulphur oxidized. Per cent.	Five hours. Average. Per cent.
$\frac{1}{100}$ normal..	0.60	0.59	0.82	0.77	1.05	1.05	1.09	1.19	1.28	1.29
	0.57		0.71		1.06		1.30		1.31	
1 per cent...	1.06	0.67	1.44	1.13	2.27	1.25	1.25	1.27	1.46	0.85
	0.29		0.83		0.24		1.28		0.25	
3 per cent...	1.45	1.31	1.36	1.26	1.61	1.53	1.56	1.57	1.24	1.59
	1.18		1.16		1.45		1.59		1.95	
5 per cent...	1.12	1.40	1.25	1.33	1.36	1.41	1.74	1.77	1.70	1.73
	1.68		1.40		1.46		1.80		1.75	

The foregoing results will be more significant if compared with the results of similar experiments made with related minerals. As already noted, experiments on the chemical behavior of pyrite

and marcasite have been conducted in this laboratory recently, and from the average results of the action of potassium permanganate on the above two minerals I have been enabled to compile a comparative table in which they are compared with my results on arsenopyrite. In order to compare the action of the permanganate on the sulphur of these three minerals on equal terms, I have calculated from Brown's tabulated results of average amounts oxidized the percentage of the contained sulphur oxidized, and doing the same for my averages on arsenopyrite have combined these calculated percentages in a table in which the action of varying strengths of solution for varying times on the three minerals can be seen at a glance.

(3) TABLE SHOWING PERCENTAGE OF THE CONTAINED SULPHUR OXIDIZED BY POTASSIUM PERMANGANATE IN ARSENOPYRITE (A),[1] PYRITE (P),[2] AND MARCASITE (M).[2]

		Strength of Permanganate Solution.							
		1/80 normal. 22°.	One per cent. 22°.	Three per cent. 22°.	Five per cent. 22°.	1/80 normal. 100°.	One per cent. 100°.	Three per cent. 100°.	Five per cent. 100°.
One hour...	A	1.69	2.12	2.75	1.45	2.98	3.44	6.66	7.11
	P	1.46	3.20	4.78	5.19	7.59	11.31	11.74	14.91
	M	2.01	2.29	5.25	4.33	5.94	12.06	12.13	15.52
Two hours..	A	1.73	1.41	1.83	2.61	3.89	5.74	6.14	6.74
	P	2.19	2.68	4.26	5.79	8.85	13.09	12.81	14.10
	M	3.48	2.27	4.18	6.39	7.20	11.12	14.94	15.52
Three hours.	A	2.03	2.01	1.98	2.24	5.32	6.37	7.77	7.14
	P	2.59	3.49	5.25	5.19	6.29	15.71	12.77	18.47
	M	3.82	3.86	5.38	6.18	7.04	16.05	17.66	24.88
Four hours.	A	2.66	3.74	6.58	2.24	6.04	6.43	8.00	8.88
	P	3.26	3.46	4.78	5.42	(3.82)	11.46	20.12	22.24
	M	(2.34)	4.35	5.40	5.92	10.56	13.87	18.37	27.84
Five hours..	A	2.01	1.81	2.52	2.36	6.61	4.33	8.08	8.76
	P	3.22	3.37	4.78	5.66	10.57	12.90	20.77	28.09
	M	4.46	4.20	5.25	7.08	10.51	17.06	(14.16)	30.67

From the above table a plat has been made to show the rates of oxidation of sulphur in arsenopyrite by different strengths of potassium permanganate solutions acting for different times, the results obtained by each strength of solution being combined into a continuous curve (Plate I). The points already mentioned above as to the action of different strengths of solution

[1] Calculated from averages as given in Tables (1) and (2).

[2] Calculated from average results as given by Brown in "A Comparative Study of the Chemical Behavior of Pyrite and Marcasite." *Proc. Amer. Philos. Soc., 1894.*

are here graphically shown. A large value has been given the vertical component (percentage oxidized) in order to separate the curves more fully.

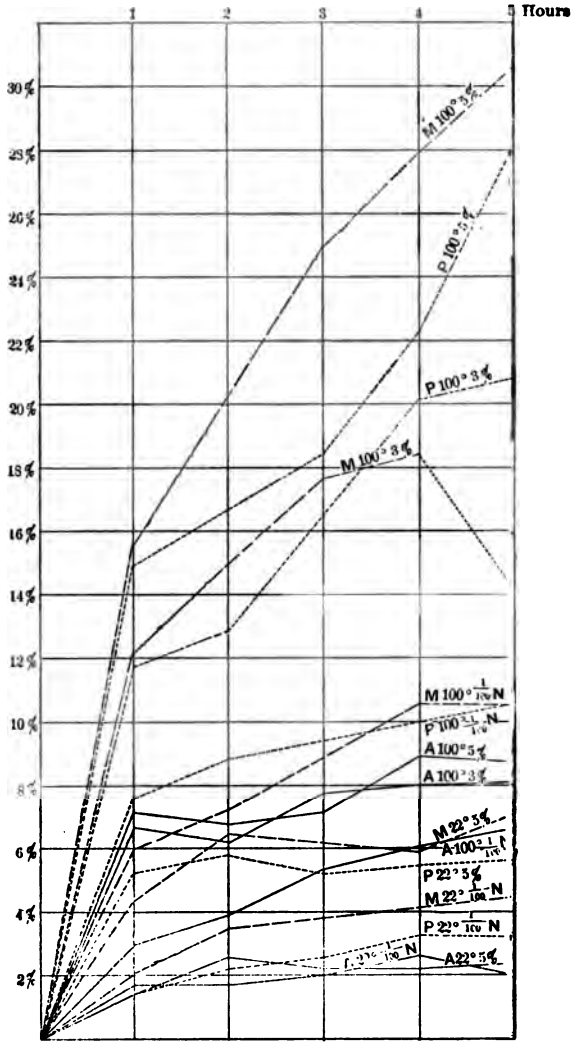


PLATE I.

A comparative plat is also given (Plate II) of selected results from table (3) in which only those curves for arsenopyrite are

selected which present a reasonable degree of regularity. They are not, however, necessarily the best in the pyrite-marcasite series.

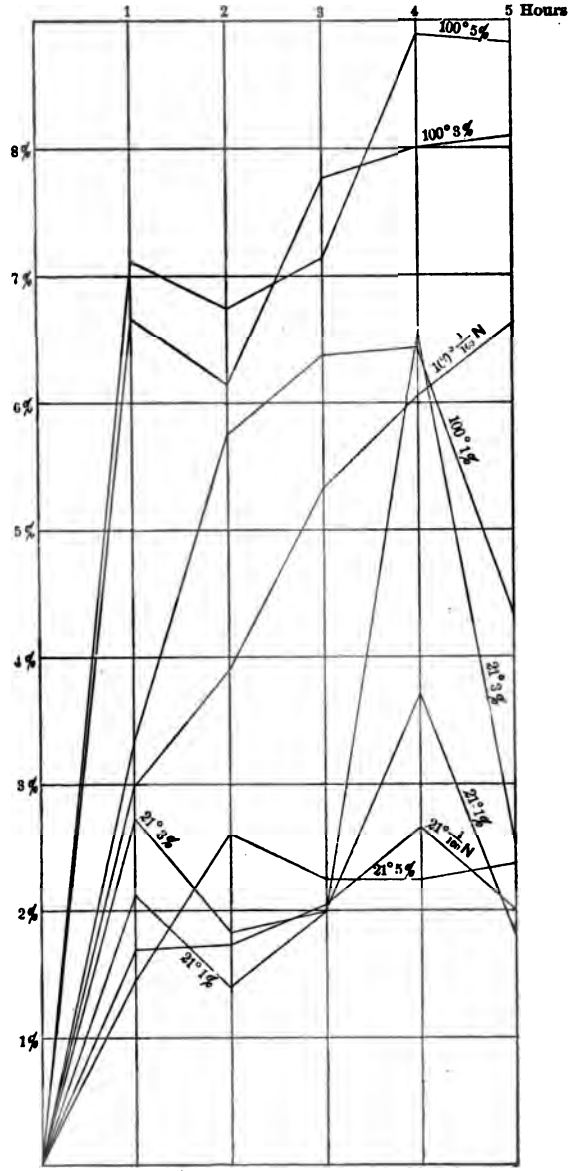


PLATE 2.

A smaller value is here given to the vertical component than in the last case in order that the pyrite and marcasite curves may be platted in full, as they rise so much higher than the arsenopyrite curves. It would be natural to suppose that the curves of arsenopyrite would be more comparable to those of marcasite than to those of pyrite on account of the isomorphism shown by their crystals, and an inspection of the platted curves will show that this is in general, correct. Take for instance the curves showing the action of $\frac{1}{100}$ normal solution of permanganate at ordinary temperature (marked A, 22°, $\frac{1}{100}$ N, etc.); it is seen that at two, three, and five hours the per cent. of oxidation of the contained sulphur in marcasite is almost exactly double that for arsenopyrite. The same condition of affairs is seen on comparing the $\frac{1}{100}$ normal solutions at 100°. It has already been noted that with the more concentrated solutions of permanganate at 100° the greater part of the oxidation of the arsenopyrite has taken place at the end of the first hour, but in the case of the pyrite and marcasite this is not the case. Their curves of oxidation rise rapidly for the three per cent. and five per cent. solutions, and are hence not comparable to those of arsenopyrite. The entire results given in table (3) are not platted here as they would simply confuse those already shown, but those obtained in the cold would serve to further illustrate the comparison that has been made between arsenopyrite and marcasite. The fact above illustrated that the sulphur in marcasite oxidizes twice as rapidly as that in arsenopyrite is what we might expect from the formula of the two minerals, marcasite being FeS_2 and arsenopyrite FeSAs.

Action of Hydrochloric Acid Gas on Arsenopyrite at Elevated Temperatures.—Experiments on the removal of sulphur from arsenopyrite by the action of hydrochloric acid gas at elevated temperatures were tried in the following manner. Two-tenths of a gram of the finely ground mineral, weighed out in a porcelain boat were subjected to the action of a stream of dry hydrochloric acid gas for one, two, and three hours at 300° and 325°, the temperatures being graded by the melting points of various salts. The sulphur in the material remaining in the boat after the action of the hydrochloric acid was determined as barium

sulphate, and the amount lost estimated by difference. While no very large amounts of sulphur were removed in this way (except in one case) the amount of arsenic driven off in the process seemed to be considerable, a large sublimate of metallic arsenic forming in the tube, and some passing out with the stream of gas. As will be seen from the results as given in the table (4) the difference in temperature between 300° and 325° caused a marked difference in the amount of sulphur removed. The temperature called 300° was between the melting points of acid sodium sulphate, $NaHSO_4$, and sodium nitrate $NaNO_3$; that called 325° was between sodium nitrate, $NaNO_3$, and potassium chlorate, $KClO_3$. The boats containing the mineral were heated in glass tubes so that the reaction could be watched. The amounts of sulphur removed at the lower temperature show no notable increase between the second and third hour, while those at the higher temperature show rapid increase of sulphur lost with the increase of time, perhaps indicating a critical temperature for the reaction of hydrochloric acid with the mineral. A comparison of these results with those obtained by Brown[1] for pyrite and marcasite is given in the table, the results being calculated to percentage of contained sulphur.

(4) TABLE SHOWING RELATIVE AMOUNTS OF SULPHUR REMOVED FROM ARSENOPYRITE, PYRITE AND MARCASITE BY ACTION OF DRY HYDROCHLORIC ACID GAS AT ELEVATED TEMPERATURES.

	One hour.		Two hours.		Three hours.	
Mineral.	Amount of sulphur removed.	Percentage of total sulphur.	Amount of sulphur removed.	Percentage of total sulphur.	Amount of sulphur removed.	Percentage of total sulphur.
Arsenopyrite, 300°	1.10	5.56	1.84	9.32	1.86	9.42
Pyrite, 300°	10.73	20.10				
Marcasite, 300°	7.19	13.48				
Arsenopyrite, 325°.....	1.62	8.29	2.82	14.29	12.21	61.78
Pyrite, 325°					17.13	32.12
Marcasite, 325°.....					10.70	20.06

Action of a Solution of Copper Sulphate Under Pressure on Arsenopyrite.—A single experiment on the action of copper sulphate in water solution on this mineral was tried by heating two-tenths of a gram of the finely ground mineral with a dilute solution of the salt in a sealed glass tube for six hours at a temperature approximating 200°. But little ferrous iron was found in

[1] Op. cit.

the solution, which seems to indicate that the iron present in the mineral is ferric. Some crystalline green arsenate (?) of copper was observed in the tube.

The results of the oxidation experiments detailed in this paper seem to bear out the relationship between arsenopyrite and marcasite indicated in the isomorphism of the two minerals, but the arsenic seems to be a disturbing element which fixes a limit, at an early stage of the oxidation, to further action of any given strength of the oxidant. The experiments with hydrochloric acid gas seem again to show the disturbing action of the arsenic present, which, at the higher temperature at least, is probably removed by heat alone, as is the case with the majority of diarsenides, leaving finally a compound readily acted on by the hydrochloric acid as shown by the large amount of sulphur removed in the three-hour's experiment at 325°. The results of this series of experiments are, therefore, not very significant as compared with those for pyrite and marcasite as given in Brown's paper. If, as indicated by the oxidation experiments, the arsenopyrite is rather to be compared with marcasite, in which Brown has shown that the iron is in the ferrous condition, we may look on arsenopyrite as a ferrous compound, but this conclusion seems to be negatived by the result of the single experiment of decomposing the mineral in a solution of copper sulphate under pressure. In this experiment it will be remembered, no considerable amount of ferrous iron was found. Further research in this latter direction must be made before definite statements as to the constitution of arsenopyrite can be formulated.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

THE PROTEIDS OF THE KIDNEY BEAN.[1]

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

THE only work on the proteids of the kidney bean having importance at the present time, is that of Ritthausen. This investigator in 1883, stated[2] that the extract of the white bean

[1] Reprinted from the report for 1893 of the Connecticut Agricultural Experiment Station, New Haven.

[2] *J. prakt. Chem.*, 103, 204.

which has a weak alkaline reaction, and is extremely difficult to filter, when made clear by subsidence, yields on adding acetic acid, a voluminous precipitate, amounting to about eleven per cent. of the seed, having the following composition:

Carbon	51.48
Hydrogen	7.04
Nitrogen	14.40
Sulphur	0.42
Oxygen	26.66
	100.00

In 1884, Ritthausen[1] published the results of further study of this seed. He then stated that the proteid, obtained in his earlier experiments, was wholly insoluble in five per cent. sodium chloride solution, but partially dissolved in two per cent. brine, and by diluting was precipitated in a form entirely like the original substance. By treating the bean meal with alcohol he found that clarification of the extracts was greatly facilitated and he, therefore, used meal so treated in his subsequent experiments.

By extraction with two per cent. sodium chloride solution, and clearing the extract by subsidence, he obtained, in two cases, precipitates of proteid, amounting respectively to 13.2 and 11.45 per cent. of the meal. Another preparation, equal to 8.67 per cent., he obtained from an aqueous extract of the meal precipitated with hydrochloric acid, the precipitate being redissolved in potash water and the solution neutralized after filtering clear. By extracting the bean meal with dilute hydrochloric acid, he obtained 10.07 per cent. of proteid. Preparations made by precipitating aqueous solutions with hydrochloric acid and sodium chloride extracts by dilution and submitting the precipitates to analysis without re-solution and consequent purification, had a composition similar to that found for the earlier preparations.

The precipitate obtained from hydrochloric acid solutions, had a different composition, agreeing with that of the proteid extracted by dilute salt solution both from the older preparations and from the freshly formed precipitate produced by acids in the aqueous extract, as well as with that of the insoluble portion remaining after this extraction, and also with that of the

[1] *J. prakt. Chem.*, N. Folge, 29, 452.

precipitate produced by hydrochloric acid in the aqueous extract, redissolved in dilute potash water and precipitated by neutralization. An average of five quite closely agreeing analyses of the proteid thus obtained, is shown by the following figures:

Carbon	52.55
Hydrogen	7.09
Nitrogen	16.18
Sulphur	0.43
Oxygen	23.75
	100.00

This proteid, Ritthausen remarked, "is so similar in composition to albumin, that one might be led to regard it as an albumin, low, indeed, in sulphur." In most respects the experiments of the writer now to be detailed, confirm these observations of Ritthausen, but in two particulars his statements have not been corroborated. The reaction of the aqueous extract, I have found in all cases, to be distinctly acid, even when the beans were tested within two minutes after crushing. Ritthausen's statement that his earlier preparations were wholly insoluble in five per cent. solution of sodium chloride, while a very considerable quantity was dissolved by two per cent. brine, is difficult to understand, unless as implied, though not directly so expressed, the presence of the proteid was detected by largely diluting the salt-water extracts. The writer has found that strong saline solutions, unless containing a large proportion of this proteid, are not precipitated by dilution, the salt being present in sufficient quantity to serve as a solvent for the diminishing percentage of the dissolved proteid.

I have been able to identify and obtain in a state of comparative purity, two distinct proteids, one, the most abundant, having quite the properties of a globulin, which I shall designate *phaseolin* and another, not so definite in character, that may be distinguished as *phaselin*.

Preparation of Phaseolin.

An extract was prepared by treating 500 grams of freshly ground bean meal,[1] which had been previously exhausted with ether, with one liter of two per cent. sodium chloride solution.

[1] The "White Medium Field Bean," the seeds being about ⅝ inch or one cm. in length, was used for this investigation.

The residue was strained out on coarse linen squeezed dry in a screw press, and again treated with a liter of the two per cent. salt solution. The resulting extract filtered very slowly and not wholly clear; about nine-tenths of it was finally obtained as a turbid filtrate. This was saturated with ammonium sulphate and the precipitate produced collected on a filter and separated as completely as possible from the solution. This precipitate was removed from the filter and treated with water. Much of the substance went into solution, but a considerable part remained undissolved. After twenty-four hours filtration, a very nearly clear liquid was obtained, amounting to about two-thirds of the solution. This was then dialyzed in a stream of river water for six days. When thus freed from chlorides, the contents of the dialyzer were transferred to a filter, but only a part of the separated proteid remained on the paper, the filtrate being milky. The precipitate collected was washed with water, alcohol and ether, and when dried over sulphuric acid, weighed sixteen grams. This preparation had the following composition:—1.

PHASEOLIN, PREPARATION 1.

	I.	II.	Average.	Ash-free.
Carbon	51.73		51.73	52.23
Hydrogen	6.89		6.89	6.95
Nitrogen	16.28	16.14	16.21	16.37
Sulphur	0.68	0.54	0.61	0.62
Oxygen				23.83
Ash	0.96		0.96	
				100.00

As this preparation separated from a not perfectly clear solution, and therefore, presumably, was impure, a part of it was dissolved in one per cent. sodium chloride brine and precipitated by dilution. After standing a few hours to settle, the precipitate was filtered off and washed with distilled water, with alcohol and with ether. Its composition is as follows:—2.

PHASEOLIN, PREPARATION 2.

		Ash-free.
Carbon	52.35	52.60
Hydrogen	6.63	6.69
Nitrogen	16.42	16.56
Sulphur	0.63	0.63
Oxygen		23.52
Ash	0.82	
		100.00

Another preparation was made by treating the fine ground beans, previously extracted both with ether and alcohol, with ten per cent. sodium chloride solution, as long as any proteid was removed. The extract was allowed to stand over night and the very nearly clear, greenish-yellow liquid was decanted from the sediment and saturated with ammonium sulphate. The precipitated proteid was collected on a filter and dissolved in dilute salt solution. This liquid was filtered as clear as possible and then dialyzed. When freed from chlorides, the globulin which had separated was filtered off, and washed and dried in the usual manner. This preparation, 3, had the following composition:

PHASEOLIN, PREPARATION 3.

	I.	II.	Average	Ash-free.
Carbon.....	52.19		52.19	52.60
Hydrogen.....	6.67		6.67	6.72
Nitrogen.....	16.01	16.06	16.04	16.17
Sulphur.....	0.63		0.63	0.63
Oxygen				23.88
Ash.....	0.79		0.79	
				100.00

As this preparation, 3, separated from a solution which could not be filtered perfectly clear, it is undoubtedly impure. In order to determine whether the preparations thus far obtained were mixtures of two or more globulins, the following were made by fractionally precipitating the extracts. The extraction was also carried out in such a way as to afford an approximate determination of the amount of phaseolin contained in the extracts.

One hundred grams of bean meal were treated with 500 cc. of one per cent. sodium chloride solution, strained through cloth, and allowed to stand so as to deposit most of the suspended matter. The solution was then decanted and 350 cc. of nearly clear extract obtained, being, therefore, approximately seven-tenths of the whole. This solution was then diluted with 1,050 cc. of distilled water and allowed to stand until the precipitate so produced had settled. The latter was collected on a filter, washed with alcohol and ether, and when air-dried was found to weigh 4.76 grams; preparation 4. The filtrate from 4 was diluted with about an equal bulk of water and carbon dioxide was

passed through it. After standing some time, a precipitate settled out, leaving the liquid nearly clear. This was decanted and the precipitate collected on a filter and treated like 4. This gave preparation 5, which weighed 3.76 grams. The filtrate from 5 was further diluted with a considerable quantity of water and carbon dioxide again passed through the solution. This gave preparation 6, weighing, air-dry, 1.12 grams. The filtrate from 6 was treated with acetic acid, and a further small precipitate, 7, obtained, weighing 0.7 gram. The four preparations together weighed 10.34 grams, and as they were obtained from seven-tenths of the total extract, were approximately equivalent to the proteid derived from seventy grams of air-dry bean meal or to 14.77 per cent. of the meal. It is evident that in preparing the globulin by dialysis in the manner just described, only a part was obtained. As preparation 4 was separated from an unfiltered extract, it was necessary to dissolve and reprecipitate it before submitting it to analysis. It was accordingly treated with one per cent. sodium chloride solution, but had become largely insoluble in brine. The insoluble matter was filtered off, the clear filtrate diluted, and carbon dioxide passed through it as long as globulin was precipitated.

The precipitate was filtered off, washed thoroughly with water, alcohol, and ether, and dried over sulphuric acid. Only one gram of proteid, preparation 4, was recovered.

PHASEOLIN, PREPARATION 4.

	I.	II.	Average.	Ash-free.
Nitrogen	16.05	15.89	15.97	16.12
Ash	0.93		0.93	

Analyses of the other preparations gave the following results:

PHASEOLIN, PREPARATION 5.

	I.	II.	Average.	Ash-free.
Carbon	52.14		52.14	52.54
Hydrogen	6.78		6.78	6.83
Nitrogen	16.35		16.35	16.48
Sulphur	0.62	0.53	0.58	0.58
Oxygen				23.57
Ash	0.77		0.77	
				100.00

PHASEOLIN, PREPARATION 6.

		Ash-free.
Nitrogen	15.83	16.23
Ash	2.51	

PHASEOLIN, PREPARATION 7.

		Ash-free.
Nitrogen	16.70	16.87
Ash	1.04	

A larger quantity of meal was next extracted, and the extract fractionally precipitated in the following manner:

Five hundred grams of meal were treated with 1,500 cc. of one per cent. sodium chloride solution, and the extract filtered once through good filter paper. About two-thirds of the extract were thus obtained as a turbid solution. Three volumes of distilled water were added, and the large precipitate formed was designated A. Through the filtrate from A, a current of carbonic acid gas was passed, and the resulting precipitate filtered off and marked B. Precipitate A was treated with about fifty cc. of ten per cent. sodium chloride brine and filtered as well as possible. A considerable part of A had become insoluble, and the filtration was exceedingly slow. After two and one-half days, most of the solution had filtered very nearly clear. This was then diluted with about ten times its volume of water, and the precipitate thereby produced, filtered off, washed with alcohol and ether, and dried over sulphuric acid; preparation 8. The filtrate from 8 was again diluted with a large quantity of water and a second precipitate obtained in a like manner; preparation 9.

The filtrate from 9 gave a very small additional precipitate with carbon dioxide, weighing, when dry, only 0.2 gram. A portion of precipitate B was dried and marked preparation 10. Five grams of precipitate B were dissolved in one-half per cent. sodium chloride solution, previously heated to 70°, filtered hot from the considerable insoluble matter, an equal volume of water heated to 70° was added to the filtrate, and the solution very slowly cooled. The proteid separated in well-developed spheroids. When this precipitate was filtered off and washed with water, the substance began to dissolve, as the salts were washed out, in the same way as the globulins of the oat kernel, castor bean, and hemp-seed dissolve, when they are washed with water, after separating from warm salt solutions on cooling. Alcohol was then added to the contents of the funnel, and the substance washed with alcohol and ether, and dried. This preparation, 11, weighed two grams.

The insoluble proteid filtered from the solution which yielded 11, was dissolved in two-tenths per cent. potash water and after filtering, the solution was exactly neutralized with two-tenths per cent. hydrochloric acid. The precipitate, which was very readily soluble in dilute sodium chloride solution, after washing with water, alcohol and ether, and drying, weighed 0.65 gram; preparation 12.

Another portion of precipitate B weighing 3.35 grams, was treated with one-half per cent. sodium chloride brine, and heated to 70°. The insoluble matter was filtered off, washed with hot dilute salt solution, with water, alcohol and ether, and when dried formed preparation 13, weighing 1.16 gram. The dissolved proteid separated from the filtrate and washings of 13 on gradually cooling, and after washing with dilute alcohol, absolute alcohol, and ether, gave 1.54 grams of preparation 14. All were then dried at 110°, and analyzed with the following results:

PHASEOLIN, PREPARATION 8.

	I.	II.	Average.	Ash-free.
Carbon	52.31		52.31	52.72
Hydrogen	7.18		7.18	7.24
Nitrogen	16.32	16.32	16.32	16.45
Sulphur	0.67	0.66	0.67	0.67
Oxygen				22.92
Ash	0.80		0.80	
				100.00

PHASEOLIN, PREPARATION 9.

		Ash-free.
Carbon	51.89	52.35
Hydrogen	6.83	6.89
Nitrogen	16.37	16.52
Sulphur, Oxygen		24.24
Ash	0.88	
		100.00

PHASEOLIN, PREPARATION 10.

	I.	II.	Average.	Ash-free.
Carbon	51.89	51.98	51.94	52.74
Hydrogen	6.84	6.64	6.74	6.84
Nitrogen	16.40		16.40	16.65
Sulphur	0.63		0.63	0.64
Oxygen				23.13
Ash	1.52		1.52	
				100.00

PHASEOLIN, PREPARATION 11.

		Ash-free.
Carbon	52.34	52.49
Hydrogen	6.78	6.80
Nitrogen	16.80	16.85
Sulphur } Oxygen }		23.86
Ash	0.30	
		100.00

PHASEOLIN, PREPARATION 12.

		Ash-free.
Nitrogen	16.54	16.67
Ash	0.81	

PHASEOLIN, PREPARATION 13.

		Ash-free.
Carbon	52.76	53.06
Hydrogen	6.81	6.85
Nitrogen	16.59	16.68
Sulphur } Oxygen }		23.41
Ash	0.57	
		100.00

PHASEOLIN, PREPARATION 14.

		Ash-free.
Carbon	52.12	52.49
Hydrogen	6.68	6.73
Nitrogen	16.33	16.45
Sulphur } Oxygen }		24.13
Ash	0.72	
		100.00

These results show that the greater part of the proteid extracted by sodium chloride solution, consists of a single globulin, amounting at least to fifteen per cent. of the seed. The greater part of the proteid remaining in the seed after extraction with salt solution, is presumably the same globulin, possibly inclosed in the tissue of the coarsely ground seed, so that it was not reached by the salt solution, or more likely, an insoluble or "albuminate" form of this globulin, as the following experiment indicates. After complete exhaustion with ten per cent. sodium chloride brine, of the meal from which preparation 3 was obtained, the residue was extracted with two-tenths per cent.

potash water, the extract allowed to stand over night and then decanted and precipitated with hydrochloric acid, added in very slight excess. The precipitate was washed by decantation, redissolved in potash water and filtered clear. This solution was then precipitated by hydrochloric acid, and as the proteid separated imperfectly, it was treated with alcohol and ether, and filtered off. After washing with dilute alcohol, absolute alcohol and ether, it was dried and analyzed; preparation 15.

PHASEOLIN, PREPARATION 15.

		Ash-free.
Carbon	51.57	52.47
Hydrogen	6.78	6.90
Nitrogen	15.71	16.00
Sulphur, Oxygen		24.63
Ash	1.72	
		100.00

Another preparation of the globulin was made by treating 100 grams of bean meal, previously extracted with ether, with 500 cc. of *distilled water*, straining through a cloth, allowing the extract to stand over night to deposit suspended matter and decanting the slightly turbid liquid, of which the 250 cc. thus obtained were diluted to 2,000 cc. and treated with a current of carbonic acid gas. On standing, the considerable precipitate settled out so that the solution could be filtered. The precipitate was washed with water, alcohol, and ether, and when dried over sulphuric acid weighed 5.5 grams. As the extract employed, measured one-half the volume of the water applied to the meal, the yield of globulin was in this case approximately eleven per cent. of the bean meal. Although precipitated from a somewhat turbid solution, and consequently not quite pure, this preparation was analyzed with the following results:

PHASEOLIN, PREPARATION 16.

	I.	II.	Average.	Ash-free.
Carbon	52.48	52.49	52.49	53.22
Hydrogen	6.71	6.86	6.79	6.86
Nitrogen	16.32	16.18	16.25	16.48
Sulphur	0.45	0.48	0.47	0.48
Oxygen				22.96
Ash	1.53	1.27	1.40	
				100.00

It is evident from this analysis that the principal proteid extracted by water, is the same as that extracted by saline solutions, and as this substance is precipitated from the aqueous extract by dilution, it is undoubtedly dissolved by aid of the salts contained in the beans. It is not probable that the acid contained in the seed causes this solution, for in that case the proteid would not be precipitated by dilution, a considerable excess of acid being necessary to effect its precipitation. The meal after extracting with water, as just described, was treated with one per cent. sodium chloride solution, the extract filtered, largely diluted with water, and charged with carbon dioxide. Only a trifling precipitate resulted which, when prepared in the usual manner, weighed 0.52 gram. This preparation, 17, ash-free, contained 16.29 per cent. of nitrogen. These results show that nearly, if not quite as much of the globulin is extracted by water with help of the salts of the seed, as by use of stronger salt solutions.

[TO BE CONTINUED.]

A NEW AUTOMATIC PIPETTE.[1]

BY EMIL GREINER.



WHEN taking a great number of samples in succession of the same volume of the same liquids, it is quite desirable to have a measuring instrument which will automatically take up the exact volume of liquid, without having to draw the same by mouth and watch for the mark, as is done when using the ordinary volumetric pipette. Therefore, I have devised an automatic pipette for such purposes, which is at present successfully employed in connection with the Babcock milk test. A glance at the accompanying cut will explain the practical value of this instrument, and as the pipettes can be made in all sizes required up to 50 cc., it can be adopted in many instances, where pipettes are used often and where accuracy is desired.

[1] Read before the New York Section, March 9, 1894.

NEW BOOKS.

AN ELEMENTARY MANUAL OF CHEMISTRY. BY FRANK H. STORER, AND WILLIAM B. LINDSAY, BEING A REVISION AND REWRITING OF PROFESSOR W. R. NICHOLS' ABRIDGMENT OF ELIOT AND STORER'S MANUAL. pp. 453. New York, Cincinnati, and Chicago: American Book Company. 1894. Price, $1.20

This work, which as the authors aptly put it, "is the lineal descendant of the Eliot and Storer Manual and the Nichols' Elementary Manual," will be greeted by its former acquaintances with the consideration due the scion of an ancient family. To those who knew not its antecedents, may be said, "it is not written in the interest of any particular theory or of any one system of nomenclature or of notation." Starting with the physical and chemical changes familiar to every one, the air and the water—mixture and chemical compound—the elementary substances composing them are studied and with these the elements naturally grouped with them. Following these are chapters upon theory, the non-metals, the metallic elements, and the periodic law, closing with an admirable appendix upon chemical manipulation, a subject too often neglected.

Nearly one hundred pages have been added to the abridgment, largely to the theoretical and physico-chemical parts, which in the former edition were conceded to be scantily treated, although there is scarcely a chapter of the descriptive part to which important additions have not been made. The sections upon chemical calculations, atomic and molecular weights, Avogadro's law, empirical and rational formulas are clearly and concisely written and should present little difficulty to the student.

The book is peculiar in the attention paid to organic chemistry, which one hardly expects to find in a manual of this kind, nearly one fourth of the volume being devoted to this branch. The topics of flame and combustion, isomerism and the three important "series" of organic compounds are carefully explained and illustrated, closing with a chapter upon "some carbon compounds derived from plants and animals" embracing the sugars and allied bodies, the principal alkaloids and dyes and a few

pages upon physiological chemistry. Nor have the newer methods of industrial chemistry been overlooked, as for example, the Solvay process and the bi-sulphite process of paper manufacture; a brief outline of the metallurgical treatment of all the metals which are technically important, is also a valuable addition.

Some may note the brevity of the account of the action of nitric acid upon the metals, and regret the omission of the Raoult method of the determination of the molecular weight by the lowering of the freezing point, and notice some points in which the old usage has been adhered to, as for example the Chevreul explanation of the action of soap, and the symbol of arsenious oxide given as As_2O_3.

The work, however, leaves little to be desired as a text-book of general chemistry in our higher institutions of learning and cannot fail to be of more than ordinary interest to the general reader. A. H. G.

NOTES.

THE CHEMICAL MIDWINTER FAIR CONGRESS AT SAN FRANCISCO.

The great success of the international congress held in connection with the World's Fair at Chicago, in August, 1893, was probably the stimulating cause which led the chemists of the Pacific coast to organize a similar congress in connection with the San Francisco Midwinter Fair. The committee in charge of the congress consisted of Prof. W. B. Rising, chairman, Professors E. W. Hilgard, John M. Stillman, G. M. Richardson, A. L. Lengfeld and Messrs. W. M. Searby, Alfred Ropp, Edmond O'Neill, Harry East Miller, Theodore J. Wrampelmier and E. C. Burr. The sessions of the congress were held in Golden Gate Hall, 625 Sutter street, June 7, 8 and 9, 1894.

The attendance at the meeting was most gratifying in the number of chemists, although the public, not much interested in such matters, was but sparsely represented. Unfortunately, no record was kept of those in attendance and only an estimate can be made of the total number, but this was in excess of

fifty, showing the lively interest taken by the Pacific coast chemists in the success of the meeting. Only two cismontane chemists were in attendance.

In the arrangement of the program of the congress but little attempt was made to group the topics together by subjects, but the arrangement was simply such as was thought would best fill in the time. The titles of the papers read on each day of the session follow:

THURSDAY, JUNE 7, 10 A. M.

Chairman W. B. Rising

1. Introductory Remarks James D. Phelan
2. "Industrial Applications of Chemistry" W. B. Rising
3. "A Theory of the Dissociation of the Products of Explosives" W. R. Quinan
4. "Concerning the Conversion of Mechanical Energy into Chemical Action J. M. Stillman
5. "Achievements and Aims of Physical Chemistry" J. R. Trevor
6. "Contraction of Aqueous Solutions of Acetone" Karl P. McElroy
7. "Modern Conceptions of Affinity and Valence" S. W. Young
8. "Analytical Notes" W. B. Rising
9. "Determination of Nickel in Nickel-Steel" L. R. Lenox
10. "Limitations of the Cyanide Process" C. W. Merrill
11. "Device for the Adjustment of a Balance" Frank Green
12. "Methods for Standardizing Reagents used in Acidimetry and Alkalimetry" C. G. Hopkins and G. C. Caldwell
13. "A Volumetric Method for the Determination of Sulphuric Acid" H. H. Deubam and G. C. Caldwell

FRIDAY, JUNE 8, 10 A. M.

Chairman H. W. Wiley

1. "Properties of Typical Florida Soils" H. W. Wiley
2. "Hawaiian Soils and Notes on the Chemistry of Certain Hawaiian Esculents" A. B. Lyons
3. "The Nitrogen Contents of Soil Humus" E. W. Hilgard and M. E. Jaffa
4. "Oil Tests" F. Shapely
5. "Chemical and Physical Properties of some California Vegetable Oils" W. C. Blasdale
6. "Some Characteristics of California Wines" W. H. Krug
7. "California and Nevada Shales and their Products" A.A. Cunningham
8. "Hydrocarbons of the Pyridin and Chinoline Series in California Petroleums and Asphalts" .. Dr. Frederick Salathe
9. "Saccharimetry in Medicine" A. E. Regensberger, M. D.
10. "Kryolith and its Industrial Application" Theodore Armstrong

SATURDAY, JUNE 9, 10 A. M.

Chairman Geo. C. Caldwell

1. "The Analytical Properties of Iron Phosphide and Phosphate" L. M. Dennis and B. S. Cushman
2. "The Preparation of Crystalline Chlorides by Means of Hydrochloric Acid Gas" L. M. Dennis
3. "Parapropionic and Metapropionic Aldehyde" W. R. Orndorff and Miss L. L. Balcom

4. "Determination of Alcohol in Fortified Wines"....T. J. Wrampelmier
5. "The Influence of Alum, Aluminum Hydroxide, and Aluminum Phosphate on the Digestibility of Bread"..
.....W. D. Bigelow and C. C. Hamilton
6. "Chrome Ore Industry".....H. G. Shaw
7. "The Education of the Technical Chemist".....J. M. Stillman
8. "The Teaching of Chemistry".....General Discussion

The sessions were held in the morning beginning at ten o'clock and continuing until one. After luncheon each day excursions were made in San Francisco and vicinity, to points which were of interest to chemists.

On Thursday afternoon the Pioneer White Lead and Color Works, the Golden City Chemical Works and the manufacturing establishment of Clinton E. Wonden and Co., were visited.

On the afternoon of Friday the Pacific Coast Borax Works at Alameda Point, and the chemical laboratory of the University of California at Berkeley, were the objective points. The greatest interest was manifested by the visiting chemists in the manufacture of borax. In Southern California there are immense deposits of crystallized hydrous calcium borate, the mineral known as Colmanite. This mineral is easily crushed and reduced to a fine powder in which condition it is mixed with natural sodium carbonate obtained from the alkali deserts and heated under pressure with water to cause the reaction to take place, by means of which the lime appears as a carbonate and the sodium as a biborate. The process although a simple one is quite complicated from a technical point of view, and the visitors were much interested and thoroughly entertained by the exhibition.

The new chemical laboratory of the University of California was also the object of the greatest interest and profit. This laboratory is built upon the most modern plan and combines most thoroughly, convenience for work and efficiency of ventilation. Every department of chemistry taught in the institution has a separate place in the laboratory and the desks, apparatus, storerooms and laboratories were all inspected with much pleasure.

On the afternoon of Saturday an excursion was made to the Western Sugar Refinery, formerly known as the Spreckels Sugar Refinery, which is one of the largest and most complete works of the kind in the world. The whole process of refining sugar was thoroughly explained and the building and apparatus inspected from top to bottom.

From the sugar refinery the party passed to the inspection of the Union Iron Works and the Pacific Rolling Mills. The gigantic operations of these two factories in the building of the great war ships which have been constructed and are under construction at this place, were thoroughly explained. No part of the excursion was of more interest to the chemist than this. The Union Iron Works kindly placed at the disposal of the chemists their private tug for the purpose of carrying the party from San Francisco to Potrero and return. The sail on the bay was thoroughly enjoyed by all.

On Saturday evening a delightful banquet of an informal nature was held at which forty, all I hope immortal, sat down. The festivities of the banquet were continued until a late hour.

On Monday the chemists were invited to visit the California Powder Works and the Giant Powder Co., situated near the Southern Pacific Railroad, about thirty miles from San Francisco. Not a very large number was able to accept this invitation, but those who did go were fully repaid for the trip.

There is no space here for comments on the scientific papers read, but, an inspection of the titles will show the broad scope of scientific research covered by the papers presented to the congress.

The visiting chemists received every courtesy from their San Francisco brethren, and those having the congress in charge certainly deserve the heartiest congratulations for the successful way in which they carried it to a happy conclusion.

H. W. WILEY.

ERRATUM.—Page 514, fifth line from bottom of page, for "*proof* silver, etc.," read "*pure* silver, etc."

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CONTRIBUTIONS TO THE CHEMISTRY OF CERIUM.[1]

BY L. M. DENNIS AND W. H. MAGEE.

THE mineral cerite was first found in one of the iron mines of Bastnäs, in Westmanland, Sweden. Its peculiarity was noticed as early as 1751 by Cronstedt,[2] and in 1784 it was analyzed by d'Elhuyar,[3] in Bergmann's laboratory, and was considered by these two chemists to be a silicate of lime and iron. In 1803 the mineral was again examined by Berzelius and Hisinger, and by Klaproth, and nearly at the same time, but independently, they discovered in the mineral a new oxide. Berzelius and Hisinger named the earth *ceria*,[4] after the planet Ceres which had been discovered two years before by Piazzi. Klaproth called it *ochroiterde*,[5] from its brownish-yellow color. Fortunately the former name was adopted, for the latter name would have been a misnomer, since pure cerium dioxide, as we now know it, has a pale-yellow color.

From that time to the present, cerium and its compounds have frequently been the subject of investigation, but the work of the earlier chemists is not of direct importance, since the ceria upon which they worked was, as we now know, a mixture of various oxides, chief among them being those of cerium, lanthanum, and didymium.

In 1839, however, Mosander make known a discovery of the highest importance; namely, that ceria was not a simple oxide

[1] Read at the Brooklyn Meeting, August 15, 1894.

[2] *Sv. Vet. Akad. Handl., 1751*, S. 227.

[3] *Sv. Vet. Akad. Handl., 1784*, S. 121.

[4] *Afhandl. i. Fysik, Kemi och Mineral.*, 1, 58.

[5] *A. Gehl.*, 2, 303; *Beiträge*, 4, 140.

but a mixture of at least two. The newly isolated earth he called *lanthana*, and this, in 1842, he split up into lanthana proper, and another oxide which he named *didymia*.[1]

Dating from the time of Mosander's discoveries, the results of the various investigations upon cerium acquire, of course, much greater value, but the chemistry of this element and the other rare earths has remained one of the most difficult problems in the field of inorganic chemistry, chiefly because of the great similarity in the chemical behavior of these different elements and the consequent difficulty of separating any one of them completely from the others. Naturally, then, in an experimental investigation of the compounds of cerium, the first problem to be solved is the preparation of pure ceria.

I. SEPARATION OF CERIA FROM THE OTHER EARTHS.

The ceria was extracted from allanite from Amelia County, Virginia, a large amount of this mineral having been most kindly sent to us by Professor W. G. Brown, of the Washington and Lee University.

Nineteen hundred and twenty-four grams of the finely powdered allanite was heated in large porcelain evaporators with concentrated hydrochloric acid until the supernatant liquid became dark brown. The syrupy liquid was allowed to cool and was then poured off, the residual mineral being again treated in the same manner until it became grayish-white, three treatments of about ten hours each usually sufficing. A portion of the residue was then moistened with concentrated sulphuric acid and heated until all of the acid was driven off. The white residue was thrown, in small portions at a time, into ice-water, and to the filtered solution, oxalic acid was added. No precipitate resulted showing that the treatment with hydrochloric acid had removed all of the rare earths.

The rare earth chlorides, mixed with those of iron, aluminum, calcium, etc., were then diluted and filtered. A portion of this filtrate was treated with hydrogen sulphide for twenty-four hours, the solution being kept at 70°, but no precipitate appeared. The hydrogen sulphide was then expelled by boiling, the sulphur was filtered off, and the filtrate was added to

[1] *Förh. Skand. Naturf. Stockholm, 1842*, 387; *Phil. Mag.*, 28, 241; *Pogg. Ann.*, 56, 503; *J. prakt. Chem.*, 30, 276.

the original solution. This was oxidized by nitric acid and a concentrated solution of oxalic acid was then added in excess. The pinkish-white precipitate of the rare earth oxalates was allowed to settle, and the oxalates were then washed by decantation with hot water until the supernatant liquid was colorless. They were then digested in large evaporators with one per cent. hydrochloric acid until all iron had been removed and were then dried and ignited in a muffle furnace. The reddish-brown oxides resulting weighed 410 grams, a yield of over twenty-one per cent.

The oxides were dissolved in concentrated nitric acid. To facilitate solution sulphurous acid was added to one portion and oxalic acid to another, but with no perceptible benefit in either case. There were obtained four liters of an almost syrupy solution which showed the didymium absorption bands very strongly.

Many different methods for separating the ceria from the accompanying earths have been proposed but none of them seem to yield cerium which is completely free from lanthanum and didymium unless the method proposed be many times repeated. Mosander,[1] the earliest worker upon this problem, obtained a mixture of didymia and lanthana free from ceria by precipitating the mixed chlorides with potassium or sodium hydroxide and passing chlorine through the suspended hydroxides. Cerous hydroxide is oxidized to the insoluble ceric hydroxide while the hydroxides of lanthanum and didymium are changed to chlorides and dissolve. Jolin[2] found that the treatment must be made seven times before the ceria is completely free from didymia and lanthana. Popp[3] added sodium acetate to the solution of the chlorides and ran in chlorine, the cerium being precipitated. Later instead of passing in chlorine gas he added sodium hypochlorite and boiled. Gibbs[4] boiled the mixed earths with nitric acid (1:2) having first added considerable lead dioxide. Zschiesche[5] heated the rare earth sulphates with red lead and nitric acid. In each of the last two methods ceric oxide is formed. Winkler[6] separated ceria and didymia from lanthana by adding

[1] *Phil. Mag.*, 28, 241.
[2] *Bihang till K. Sv. Vet. Akad. Handl.*, 2, 14; *Bull. Soc. Chim.*, [2] 21, 533.
[3] *Ann.*, 131, 359; *J. B.*, *1864*, 195 and 702.
[4] *Sill. Amer. Jour.*, [2] 37, 332.
[5] *J. prakt. Chem.*, 107, 65.
[6] *J. prakt. Chem.*, 95, 410.

mercurous oxide to the solution of the chlorides and then potassium permanganate until the solution is colored by the latter. Ceria and didymia are precipitated. Welsbach[1] precipitates the ceria by fractional crystallization as cerium ammonium nitrate. Bunsen first[2] proposed to ignite the oxides with magnesia, to dissolve out the ceria as cerium magnesium nitrate and then pour the solution of the latter into a large amount of very dilute nitric acid, whereby ceric oxide is precipitated. Later[3] he abandoned this method and proposed instead the method which has been most employed for preparing pure ceria. A solution of impure cerium sulphate is poured into boiling water containing one part of nitric acid to the thousand, and basic cerium sulphate is thrown down. This procedure must be repeated several times and is also very wasteful because the yield is small, so that it can be used with advantage only on material that is already nearly pure. Brauner[4] increased the yield by dissolving finally in nitric acid instead of in sulphuric acid, driving off the excess of acid and precipitating with boiling water containing nitric acid. Debray[5] fused the nitrates of the earths with from eight to ten times their weight of potassium nitrate at a temperature between 300° and 350°. The nitrate of cerium is decomposed leaving the oxide which is insoluble in water. The other nitrates are undecomposed and are soluble in water. Many repetitions were necessary to free the ceria from the other earths. Pattinson and Clark[6] heated the mixed chromates to 110° when cerium chromate decomposes to ceric oxide, the other chromates remaining unchanged.

For the separation of the ceria from the other earths in the allanite solution obtained as stated above, the authors first employed the Mosander-Jolin method which so eminent an investigator as Cleve has pronounced to be the best. The nitrate solution of the earths was diluted, potassium hydroxide was added in excess and well-washed chlorine gas was run into the solution for from four to five days. The white precipitate of

[1] *Monatsh. f. chem.*, 4, 630.
[2] *Ann.*, 105, 40.
[3] *Pogg. Ann.*, 155, 375.
[4] *Monatsh. f. chem.*, 6, 792.
[5] *Compt. rend.*, 96, 828.
[6] *Chem. News*, 16, 259.

the hydroxides soon changed to a dirty violet and became light yellow soon after the action of the chlorine began. The ceric oxide was washed by decantation until the wash-water gave no precipitate with ammonium hydroxide, this washing occupying nearly a week as the precipitate settles very slowly. The precipitate was then dissolved in hydrochloric acid and the treatment with chlorine was repeated. After seven complete treatments the concentrated solution of cerium chloride showed no absorption bands when a layer ten cm. thick was examined with a Krüss spectroscope. The solution was then nearly neutralized with ammonium hydroxide and hydrogen sulphide was run in for twenty-four hours, the solution being warmed to 70°. A very slight precipitate of copper sulphide resulted. This was filtered off, the hydrogen sulphide was expelled by boiling and the separated sulphur was removed by filtration. To the filtrate was added a concentrated solution of pure oxalic acid, a snow-white precipitate of the oxalates of the rare earths resulting. This precipitate was treated with a hot solution of hydrochloric acid (two per cent.) until the washing liquid failed to give a reaction for iron when tested with potassium sulphocyanate and ether. The oxalate was then dried and ignited in porcelain crucibles over the blast-lamp. The resulting oxide was of a pale yellow color resembling in tint very light chamois leather.

In the meantime the method of separation proposed by Debray was tried upon another portion of the rare earths. It was found that the melting point of the mixture of rare earth nitrates and potassium nitrate was usually about 325°. (The melting point of potassium nitrate is stated to be 339°.) Upon treating the fused mass with water it was found that the insoluble residue contained, even after two fusions, appreciable amounts of didymium. Since cerium nitrate begins to decompose at 200° and didymium nitrate at about 300°, the cause of the presence of didymium in the insoluble cerium oxide is evidently to be ascribed to the high melting point of the nitrate mixture employed by Debray. If then the melting point of the mixture could be lowered the probable result would be that less of the didymium nitrate would be decomposed and it seemed reasonable to expect that, by sufficiently depressing the melting point,

cerium oxide completely free from didymium might be obtained by a single fusion. With this end in view the potassium nitrate was replaced by sodium nitrate, the melting point of the latter, 316°, being somewhat lower than that of the potassium nitrate. But even with this salt more than two fusions were necessary to free the cerium from didymium.

Carnelley and Thomson[1] have shown that while potassium nitrate melts at 339° and sodium nitrate at 316°, a mixture of these two salts in molecular proportion melts at 231°. Consequently, this mixture was next tried with the rare earth nitrates, the details of the method being as follows:

The oxalates of the rare earths, after being freed from iron, as above described, are placed in porcelain evaporating dishes, the oxalates being covered by funnels of such size that when inverted they fit inside the edge of the evaporating dish. Concentrated nitric acid is now poured over the oxalates. Action begins at once in the cold, but it can be greatly hastened by warming on a water-bath. After the nitrogen oxides cease to come off, and the liquid has become clear, the solution, which should be so concentrated as to be syurpy in consistency, is poured while still hot into large porcelain crucibles half-filled with the well-ground mixture of potassium and sodium nitrates. About enough of the solution to completely cover the dry nitrates is poured in and the whole is thoroughly mixed by stirring.

For heating the crucibles a double air-bath was used. Both of the air-baths and the two covers were lined within and without with asbestos board. Through the two covers, openings were made through which thermometers could be introduced at various points within the inner bath. The crucibles were placed in circular openings cut in a piece of asbestos board, this board resting on pipe clay rods in the inner air-baths. The asbestos board was also pierced with many smaller openings to allow free circulation of air. The air-bath was heated by two Bunsen burners, the height of the flame being kept constant by means of "precision" gas-cocks.

After the crucibles have been placed in position the temperature is brought up slowly, too rapid heating being liable to cause

[1] *J. Chem. Soc.*, 53, 782.

the mass in the crucibles to swell and run over the edge. The two covers are placed in position, and a thermometer is inserted through the center opening to such a distance that its bulb is on a level with the bottoms of the crucibles. The heat is gradually increased until the thermometer shows a temperature of 300° in the inner bath. The mixture melts at a little below 230°, and decomposition of the cerium nitrate begins almost immediately. As the temperature rises the brown fumes come off copiously, the evolution gradually lessening as the heating continues. If, after removing the covers, it is seen that the evolution of gas from the fusion has entirely ceased, then the decomposition possible at the temperature employed is complete. This usually takes from four to five hours after the temperature has risen to 300°. It was found that the cerium nitrate is not entirely decomposed even when the temperature has been kept at 350° for some time, and also that if the temperature rises above 320° the cerium oxide will contain some didymium. After the evolution of nitrogen oxides ceases, the bath is allowed to cool rapidly since by so doing the solid mass can usually be removed by inverting the crucible and tapping the edge gently. If it cannot be removed in this way it can usually be loosened by throwing a jet of hot water around the upper edge. The removal of the mass in a solid block is of advantage since the condition of the decomposition may be judged by the color of the oxide which has collected at the bottom. If it is bright yellow or nearly white the ceria is probably pure, but if brownish in color then some of the didymium nitrate also has been decomposed.

The solid mass is now treated with hot water which dissolves all but the oxides. These are allowed to settle and the supernatant liquid is decanted off through a filter. More hot water containing from four to five per cent. of nitric acid is poured over the oxides and the liquid is brought to boiling and poured while hot through the filter. This is repeated six times and finally the oxides are washed with hot water alone, the washing being continued until the wash-water gives no precipitate with ammonia.

The oxides are dissolved by heating them with concentrated sulphuric acid until fumes of sulphur trioxide begin to escape,

allowing the mass to cool and then treating it with a large amount of water. More rapid solution can, however, be effected by throwing a jet of water upon the hot sulphates and stirring the mass constantly. There is some tendency to spatter, but solution is obtained in much less time and with much less water than in the first procedure. A concentrated solution of cerium sulphate thus obtained showed no didymium absorption bands in a layer thirty cm. thick.

To test the separation quantitatively, weighed amounts of pure cerium and didymium oxalates were mixed, the mixture was dissolved in nitric acid as above described and the mass was fused with the mixed alkali nitrates. The soluble portion from the first fusion was evaporated down and again fused with the alkaline nitrates, and this solution and fusion was repeated in all four times. The temperature during each fusion was about 300° The insoluble cerium oxide resulting from the fusions was in each case free from didymium, and of the total cerium taken more than sixty-three per cent. was obtained completely free from didymium by the four fusions.

Another sample of the mixed nitrates was fused at about 350°. The layer of cerium oxide which collected at the bottom of the fused mass showed a brown coloration at the edges, and the insoluble residue after being carefully washed and dissolved in sulphuric acid gave the didymium bands clearly. The filtrate tested by the hydrogen peroxide method mentioned below showed some cerium still present with the didymium.

From the foregoing it will be seen that while the method is not quantitative it is nevertheless quite rapid and the yield is comparatively high. Its chief merit lies in the fact that the cerium oxide resulting from each single fusion is free from didymium, an advantage which does not seem to be possessed by the other separation methods with which the authors are acquainted.

II. QUALITATIVE TESTS FOR CERIUM.

Early in the work the necessity arose for testing various solutions and residues for the presence of traces of cerium, and a comparison of the different methods which have been proposed was made to ascertain which test was most distinctive and delicate.

Until 1864, when Gibbs[1] proposed his lead dioxide test for ceria, no satisfactory method for the qualitative detection of this earth was known. In 1882, Hartley[2] proposed a more delicate and also a more easily applied test, using ammonium acetate and hydrogen peroxide. In 1885, Lecoq de Boisbaudran,[3] and also Cleve,[4] observed that hydrogen peroxide gave to solutions of cerium salts, to which an excess of ammonium hydroxide had been added, a precipitate of the same color as that yielded by Hartley's reagents; namely, an orange-red. Sonnenschein,[5] in 1870, had proposed the use of ceria as a test for strychnia, and Plugge[6], in 1891, has reversed this, using strychnia as a test for ceria. Finally, Gibbs[7], in 1894, has proposed to substitute bismuth tetroxide for lead dioxide in his test.

Hartley appears to have been the only observer previous to Plugge to test the delicacy of the reactions proposed. He found that if a quantity of a cerium salt, equivalent to one mgm. of the element, were dissolved in 100 cc. of water, the addition of ammonium acetate and hydrogen peroxide gave a distinctly brown or orange-red precipitate which could be filtered off, dried, ignited, and weighed. "Hence, we can separate one part of cerium from 100,000 parts of liquid."

To test the delicacy of these various reactions one-half gram of ceric oxide was dissolved, as sulphate, in a liter of water. Each cubic centimeter of this solution would contain one-half mgm. of ceric oxide. When one cc. of this solution was diluted to 100 cc., and five cc. of the diluted solution was boiled with excess of lead dioxide and nitric acid (1:2), a faint yellow tint was to be observed, but four cc. failed to yield a distinguishable color; that is, 0.025 mgm. can be detected in about seven or eight cc. The bismuth tetroxide detected 0.017 mgm. under the same conditions.

In testing Hartley's reaction, one cc. containing one-half mgm. was diluted to 100 cc., each cubic centimeter then containing

[1] *Am. J. Sci.*, [2] 37, 352.
[2] *J. Chem. Soc.*, 41, 202.
[3] *Compt. rend.*, 100, 605.
[4] *Bull. Soc. chim.*, [2] 43, 57.
[5] *Ber. d. chem. Ges.*, 3, 631.
[6] *Arch. d. Pharm.*, 229, 558.
[7] *Am. Chem. J.*, 15, 546.

0.005 mgm. of ceria. When two cc. of this solution was diluted so much that with the solution of ammonium acetate and hydrogen peroxide it formed about four cc., a yellow color was visible, especially on looking downward into the test-tube held above a white surface; 0.01 mgm. of ceric oxide, or rather the cerium salt equivalent to this, can, therefore, be detected. Ammonium hydroxide and hydrogen peroxide gave as distinct a color with one cc., that is, Boisbaudran's test is twice as delicate as Hartley's.

Next, Plugge's strychnia test was tried and proven to be as delicate as he claims. The strychnia solution is prepared by dissolving one part of strychnia in one thousand parts of sulphuric acid. The solution suspected of containing ceria, or a few cubic centimeters of it, is rendered alkaline by sodium hydroxide, evaporated to dryness, and a drop of the strychnia solution is added. One-tenth of a milligram of ceria gives a distinct blue or violet color changing to red. One-hundredth of a milligram gives a faint blue tinge which rapidly fades. If oxalic acid be present it must be decomposed or the test fails. Boisbaudran's test is then the most delicate of any yet proposed.

Finally, known amounts of lanthana and didymia (mixed) and ceria in solution were mixed and Boisbaudran's test applied. A distinct coloration of the hydroxides was produced when 0.01 mgm. of ceria was mixed with 0.1 gram of lanthana and didymia in about 100 cc. of solution.

To apply the test in the presence of a large excess of other rare earths, very dilute ammonium hydroxide solution should be employed and this added drop by drop until the first permanent hydroxide remains after shaking. The hydrogen peroxide is then to be added—only a couple of drops are needed—and the mixture well shaken. By this means the weakly basic ceria is precipitated almost alone and the orange-red color cannot be disguised.

III. CEROUS CHLORIDE.

The ceric oxide, prepared according to the directions given in the first section, was purified from any thoria present, by boiling the oxalate (prepared from the sulphate) with a concentrated solution of ammonium oxalate. Any thorium oxalate dissolved,

was poured off and a similar solution poured over the residual cerous oxalate. The whole was then bottled and allowed to stand for some months with occasional shaking. The mixture was then brought to boiling and the liquid again poured off, the residual oxalate being washed with a similar solution. This washed oxalate was then dissolved in nitric acid, care being taken to ensure full decomposition and it was then almost neutralized with ammonium hydroxide. Potassium hydronitride was then added[1] so long as it continued to throw down a precipitate. This was filtered off leaving a solution of cerium nitrate containing only potassium and ammonium salts with possibly traces of calcium. This solution was precipitated with ammonium hydroxide and washed by decantation until a liter of the wash-water left no residue on evaporation. The ceric hydroxide was then tested for calcium, potassium, etc., with the spectroscope and proved to be free from all foreign material. This pure hydroxide has been employed to prepare salts of cerium.

As this work has been in reality only preliminary to an extended study of cerium, many of the already known salts were prepared in order to become familiar with their characteristics, but of these there is no need to speak at length.

A salt, which may probably be rightly claimed to be a new compound, was prepared while endeavoring to obtain cerium tetrachloride. This latter should be capable of existence if cerium is properly placed in the periodic system. Every other element in group IV of that system forms such a chloride not even excepting lead.[2] Among other attempts made, one was as follows: A concentrated solution of cerous chloride, obtained by dissolving ceric chloride in hydrochloric acid and evaporating was placed in a wash-bottle surrounded by a freezing mixture (snow and salt) and dry chlorine gas run in. This was rapidly absorbed, and after a short time a white crystalline mass settled out. This was placed on a porous porcelain plate to remove the greater part of the liquid, and then the following experiments were tried with different portions.

An attempt was at first made to dry it to constant weight over

[1] Dennis and Kortright, *Am. Chem. J.*, 16, 79.
[2] *Monatsh f. Chem.*, 14, 505.

dry caustic potash in vacuo. A large, but irregular, loss of weight occurred and the crystals evidently effloresced. On exposing it to the open air again it gained in weight till almost as heavy as at first.

An attempt to dry it over calcium chloride gave a similar result. A portion was then dried in air, dust being excluded.

	Grams.
Weight of sample taken	2.9824
" " " after 72 hours	2.9801
" " " " 118 "	2.9790
" " " " 142 "	2.9786
" " " " 166 "	2.9786

The chloride therefore assumes a constant weight in air.

In analyzing this air-dried chloride the cerium was first precipitated from the aqueous solution of the salt by ammonium hydroxide. The precipitate was so gelatinous that it was difficult to wash it free from chlorides and the oxide obtained by ignition of the precipitate was not of a pure yellow color. The percentages of cerium obtained in two analyses were 38.01 and 38.19.

In two other samples the cerium was thrown down by ammonium hydroxide and hydrogen peroxide was added. The orange-colored hydroxide thus formed was not as gelatinous as that formed with ammonia alone, and was much more easily washed, but on ignition of the precipitate the resulting ceric oxide was of a pale pink color. This color may have been due to the presence of a small amount of a higher oxide, for the results—38.01 and 37.93 per cent. cerium—while not agreeing as well as could be wished, were too high (see analysis below). The chlorine was determined by precipitation as silver chloride and the water by the method suggested by Kraut.[1]

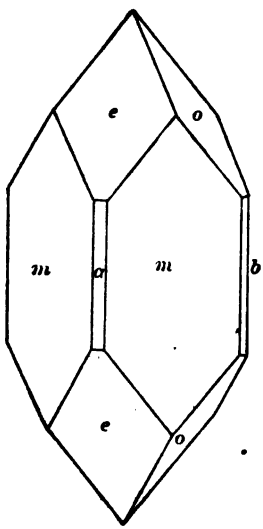
	Calculated for $CeCl_3 7H_2O$.	Found.
Ce	37.63	37.97
Cl	28.54	28.58
H_2O	33.83	33.88

The above analysis showed that the compound formed by passing chlorine into a cold saturated solution of cerous chloride was merely a finely crystalline form of cerous chloride and not a

[1] *Ztschr. anal. Chem.*, 2, 242.

ceric chloride. Inasmuch then as the formation of the compound was probably due not to the oxidizing action of the chlorine, but to its dehydrating power, it seemed reasonable to expect that dry hydrochloric acid gas would accomplish the same result. The hydrochloric acid gas was made by the action of concentrated sulphuric acid upon solid ammonium chloride, the apparatus of Norblad being used for this purpose. Upon passing the gas into a cold concentrated solution of cerous chloride, the same white finely crystalline compound separated as with the chlorine. This was dried in the air to constant weight and then analyzed. In determining the cerium, the orange-colored hydroxide was precipitated by ammonium hydroxide and hydrogen peroxide but, before filtering, the solution was heated just to boiling. The suspended hydroxide changed to a bright yellow color but it did not become gelatinous and was easily washed. On ignition it yielded a ceric oxide of the usual pale yellow color.

	Calculated for $CeCl_3.7H_2O$.		Found.	
Ce.....	37.63		37.70	37.71
Cl	28.54		28.41	28.45
H_2O	33.83	by diff.	33.89	33.84



The crystalline form of the chloride was kindly determined by Mr. A. S. Eakle, of the Geological Department of the University, who states that "the cerous chloride is orthorhombic in crystallization, and of the form shown in the figure.

The axial ratio $\breve{a}:\bar{b}:c = 0.80834:1:1.44187$.

$a = \infty P \breve{\infty}$ (100)
$b = \infty P \breve{\infty}$ (010)
$e = P \bar{\infty}$ (101)
$m = \infty P$ (110)
$o = P \breve{\infty}$ (011)

Faces.	Angles measured.	Angles calculated.
110 : 1$\bar{1}$0	77° 54′	
110 : $\bar{1}$10	102° 12′	102° 6′
101 : 011	49° 20′	"

The above chloride seems to be distinct from that obtained by Jolin[1] and by Lange[2] for which the formula $2CeCl_3.15H_2O$ is generally given.[3] That chloride may be made by dissolving ceric hydroxide in hydrochloric acid and evaporating on the water-bath until the solution becomes quite viscous. This solution placed in a desiccator while hot solidifies on cooling to a crystalline mass of a yellow color. If these crystals be allowed to stand in the air, they lose their color and a glassy coating appears to form over the surface. The differences between the results obtained by Jolin and by Lange and the variation of each of their analyses from the calculated percentages made it seem desirable to repeat the analysis of chloride prepared by Jolin's method to see if better results could not be obtained. A sample of their chloride was therefore prepared by us and analyzed, but the results showed as great a variation from the theory as those already mentioned.

	Calculated for $2CeCl_3.15H_2O$.	Jolin.	Lange.	Magee.	Calculated for $CeCl_3.7H_2O$.
Ce	36.74	36.89	37.37	36.37	37.63
Cl	27.87	28.40	28.80	28.65	28.54
H_2O	35.39				33.83

IV. THE HYDROXIDES OF CERIUM.

The peculiar color changes of the hydroxides of cerium have often been noticed by chemists who have experimented with that element. When any one of the alkaline hydroxides is added to a solution of a cerous salt a white hydroxide is precipitated. This, so most authorities state, becomes slowly yellow on exposure to the air, more rapidly if chlorine or other oxidizing agents be present. Popp,[4] however, claims that he obtained a dirty violet hydroxide by leading chlorine into a solution of a cerium salt precipitated by an acetate. This he claimed to be a higher hydroxide than the yellow. He states that it gave on ignition a red oxide. Others have claimed that his violet hydroxide was a basic acetate. Rammelsberg[5] obtained a like-colored hydroxide by precipitating a hot solution of ceroso-ceric sulphate with caustic potash. Hermann[6] and Stapff[7] also obtained

[1] *Bull. Soc. Chim.*, [2] 21, 153.
[2] *J. prakt. Chem.*, 82, 129.
[3] *Gmelin-Kraut, Dammer and others.*
[4] *Ann.*, 131, 361.
[5] *Pogg. Ann.*, 108, 45.
[6] *J. prakt. Chem.*, 30, 189; 92, 113.
[7] *J. prakt. Chem.*, 79. 257.

peculiar hydroxides to which they attempted without much success to assign formulas. Later Lecoq de Boisbaudran,[1] by the addition of ammonium hydroxide and hydrogen peroxide to a solution of a cerous salt, obtained an orange-red precipitate, which was studied by Cleve,[2] who, as a result of his observations, considered it the hydroxide corresponding to an unknown CeO_3; namely $Ce(OH)_6$.

The following observations may throw some light upon the matter. A solution of mixed chlorides, containing lanthanum, didymium, and cerium was boiled and precipitated, while hot, with ammonium hydroxide. This was done in a large bottle which could be tightly corked. The mixed hydroxides were almost perfectly white, having possibly a faint pinkish tint. After the hydroxides had settled, the supernatant liquid was poured off and the bottle was refilled with thoroughly boiled distilled water. This was repeated until all foreign salts had been removed, the bottle being kept closely stoppered except while decanting and refilling. The hydroxides suffered no change of color upon standing for some days. Therefore, cerous hydroxide and the hydroxides of didymium and lanthanum when mixed are almost white. Didymium hydroxide by itself, however, or without much intermixture of white hydroxides, has a pinkish color. Finally air was blown through the suspended hydroxides. The color rapidly changed, at first to a dull purple and finally to a pale yellow.

Next a solution of cerous chloride was treated in the same manner. The hydroxide remained perfectly white while air was excluded, but, being exposed to air, it took on a dull purple color changing later to a bright yellow. Through another similar sample, air freed from carbon dioxide was passed; the same change in color resulted. Through yet another, pure carbon dioxide was passed. It remained white and did not change to purple even when, after some time, air was substituted for the carbon dioxide, the stability doubtless being due to the complete transformation of the hydroxide to the carbonate. Through yet another sample, air from which both oxygen and carbon dioxide were removed, that is, nitrogen, was passed. It remained white. Next a bottle was about one-

[1] *Compt. rend.*, 100, 605. [2] *Bull. Soc. Chim.*, [2] 43, 57.

sixth filled with cerous chloride and this was precipitated—white—with ammonium hydroxide, and the bottle was then filled with unboiled water and lightly stoppered. The precipitate changed in color quite rapidly to light purple which gradually became darker from above downward and finally the top began to change to yellow. After about four months the upper third had become yellow, that below it being still violet.

Both the white and the purple hydroxides when washed on filter paper, dried at a low temperature and then ignited, gave an olive-green oxide, which did not become yellow even when the highest heat of the blast-lamp was applied. On powdering it very finely it seemed more nearly yellow. The weights seemed to agree well, however, with that called for by ceric oxide. The yellow hydroxide when dried and ignited gave a pale yellow ceric oxide. When the yellowish-white oxide prepared by this method or by igniting the oxalate is again ignited over the blast-lamp, but in an atmosphere of hydrogen, it becomes olive-green without marked loss of weight. For example 0.1263 gram of yellow oxide ignited in hydrogen weighed 0.1261 gram; 0.1574 gram similarly treated gave 0.1570 gram. When again ignited in air or oxygen, the oxide became yellow and regained its original weight. Bunsen[1] obtained very similar results.

As mentioned in a previous section, the precipitate obtained by the united action of ammonium hydroxide and hydrogen peroxide, on being dried and ignited, gives a pink oxide which seems to weigh somewhat more than ceric oxide, CeO_2, should.

Another point, perhaps worthy of notice, was that when some of the purple hydroxide was dissolved in sulphuric acid and allowed to stand for a few days there separated out a crystalline sulphate which, on analysis, gave results too high for cerous and too low for ceric sulphate.

It is to be concluded, then, so far as the present observations go, that cerous hydroxide is white; that on exposure to oxidizing agents including atmospheric air it becomes first purple and then yellow, or, in other words, the purple hydroxide is an intermediate product.

[1] *Ann.*, 105, 40.

CORNELL UNIVERSITY, July 7, 1894.

METHOD FOR THE DETERMINATION OF THE FREEZING-POINT OF FATTY ACIDS.[1]

By F. Wolfbauer.

Translated and Abridged by S. S. Emery.

BY reason of the lack of agreement between different chemists in the determination of the freezing-point of a fat, and also because of the commercial importance of this determination as indicating the quality of fats, it seemed desirable that a standard method for this determination should be adopted.

Accordingly, my proposed method, after being carefully examined by Dr. R. Benedikt, Dr. von Perger, Dr. Ferd. Ulzer, and myself, was agreed upon by us as the method by which all future determinations of the freezing-point should be made.

The method is as follows:

One hundred and twenty grams of the fat is melted in a beaker at a temperature but slightly above its melting-point, mixed with forty-five cc. of caustic potash solution (1,250 grams of caustic potash in one liter of water[2]), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, being occasionally stirred. A small portion is then tested by warming with alcohol (fifty per cent.) to ascertain whether saponification is complete, indicated by obtaining a clear solution; otherwise it must be replaced in the bath and there allowed to remain until this is accomplished.

The soap is now decomposed by boiling with 165 cc. of dilute sulphuric acid (sp. gr. = 1.143 = 18° B.[3]), preferably done in a silver dish, and continued until the free fatty acid rises to the top as a perfectly clear oily layer.[4] The silver dish is then covered with an evaporating dish filled with cold water, to check the evaporation. The aqueous solution is then completely drawn off, and the fatty acid washed by boiling one-quarter of an hour

[1] From the Mittheilungen des Technologischen Gewerbmuseums, Wien, 1894.

[2] This solution should have a sp. gr. of 1.509, and contain forty-eight per cent. of potassium hydroxide.

[3] Or a mixture of twenty-two cc. concentrated sulphuric acid and 150 cc. water.

[4] If the size of the dish will permit of so doing, it is recommended to add (before decomposing) 150 cc. of boiling water, and allowing to stand ten minutes at 100° C.,—whereby the soap takes up water, rendering the subsequent decomposition more rapid

with dilute sulphuric acid (five cc. of concentrated sulphuric acid and 100 cc. of water). After settling and removing the dilute acid, it is boiled with 100 cc. of pure water,—this last being repeated should the washings taste distinctly acid. It is then dried in an open dish at 100° C. for two hours.

Only fatty acids obtained as above can be considered sufficiently pure and dry to be used for the determination of the freezing-point.

In the determination proper the following apparatus is employed: A thin-walled test-tube, three and one-half cm. by fifteen cm., is fixed by means of a cork in a suitable bottle A Centigrade thermometer, extending from 1° to 60°, and graduated in fifths of a degree, is fixed in the test-tube by a second cork, which must be sufficiently loose to permit of an easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore in the interval between 2° and 28°. The amount of mercury *above* the surface of the fatty acid is thus diminished and a very appreciable error (a lowering of the freezing-point) is consequently avoided.

To accomplish the determination the test-tube is filled to within one cm., or one and one-half cm., of the top with the melted fatty acid, the thermometer immersed in the liquid to about the 35° mark (when the instrument should clear the bottom of the tube by about four cm. or five cm.), and the liquid stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed, and after stirring rapidly in a circle ten more times, the thermometer is allowed to stand. The mercury now begins to rise in consequence of the latent heat liberated from the solidifying fatty acid; the highest temperature noted may be taken as the freezing-point.

The reading of the thermometer should be corrected for its inherent errors, previously determined. Its zero point should also be redetermined from time to time.

Each freezing-point determination should be repeated, and the difference between the two should not exceed 0.1° C.; as a rule it will not exceed 0.05°.

The use of narrower test-tubes than above prescribed, as well as lack of attention to other details, generally leads to low results, as a so-called "over-cooling" always appears in the passage from the liquid to the solid state.

The experiments which justified the adoption of this method were carried out in the following lines:

I. The influence of the method of saponifying.

II. The influence of the length of time of saponifying.

III. The influence of the degree of dryness of the fatty acid.

IV. The influence of the size and shape of the vessel in which the freezing-point is determined.

V. The influence of a different length of thermometer.

I. The Effect of the Method of Saponifying.—The following determinations show that either an aqueous or an alcoholic solution of caustic potash may be used for the saponification:

	Freezing-point found by means of aqueous saponification.	alcoholic saponification.
Fatty acid I	43.00°	43.08°
Fatty acid II	43.49°	43.52°

It should be here remarked that, in the case of alcoholic saponification, a one and one-half hours' boiling of the soap solution diluted with one liter of water is necessary to completely remove the alcohol.

II. The Influence of the Length of Time of Saponifying.—The two following determinations were made on the same fat; in I the time of saponifying was limited to one and one-half hours, while in II it was prolonged to fully fifteen hours:

	Freezing-point.
Determination I	43.49°
Determination II	43.44°

It is therefore evident that a variation in the length of time of saponifying does not influence the final result.

Regarding the minimum length of time necessary, it varies with different fats,—slightly rancid fats requiring less than fresh fats, some of the former undergoing even spontaneous saponification on being mixed with the caustic potash. As a rule, however, for fresh fats two hours is amply sufficient, provided the fat was not melted at too high a temperature, and that, after

adding the caustic potash, a perfect emulsion was obtained by a vigorous stirring.

III. The Influence of the Degree of Dryness of the Fatty Acid.—Comparative tests have shown most conclusively that by increasing the amount of water in a fatty acid the freezing-point is lowered, and *vice versa*. Further, as the absorbent power of fatty acids for water is less in the cold than at a higher temperature, it follows that during the cooling of a fatty acid, saturated with the maximum amount of water, at a certain temperature a separation of water must take place, shown by the still liquid fatty acid becoming turbid. This turbidity naturally interferes with the detection of solidification, and consequently, determinations made on undried or partially dried fatty acids show much less agreement with each other than those made on the perfectly dried acid. In two determinations on the same fat, using the undried fatty acid, were obtained the

freezing-points	43.14°
and	42.86°
the freezing-points differing by	0.28°

If, after washing a fatty acid, a filtration be substituted for the drying, a partial removal of the water is thus effected. But as the freezing-point of a fatty acid so treated is 0.3°–0.4° lower than one similarly treated, but also dried, it appears that such a filtration is entirely superfluous.

As is shown in the following table, it makes no difference in the final result whether the fatty acid be dried only one and one-half hours or a much longer time. It is also immaterial whether the dried fatty acid be used immediately for the determination, or whether it be first allowed to solidify and to stand a long or short time, being subsequently remelted for the determination.

RESULTS OF A SERIES OF DETERMINATIONS OF THE FREEZING-POINT OF A FATTY ACID, BY AQUEOUS AND ALCOHOLIC SAPONIFICATION, AND USING THE DRIED FATTY ACID.

Determination. No	The saponification effected with	and continued.	Further treatment of the fatty acid.	Freezing-point found.	Difference from the average.
1.	Aqueous potash....	15 hours....	Dried 5 hours....	44.44°	—0.02°
2.	" "	1½ "	" 4 "	43.49°	+0.03°
3.	A mixture of the above two dried fatty acids, washed again with water, filtered, and then dried two hours.			43.35°	—0.11°

4.	The fatty acid from the above test after standing twelve hours in the solid state, and then heated one hour.			43.51°	+0.05°
5.	Alcoholic potash...	½ hour.....	Filtered and dried one hour.	43.52°	+0.06°
6.	Aqueous " ...	3 hours....	Not filtered, dried two hours.	43.45°	—0.01°
7.	" " ...	The fatty acid from the above test after solidifying, immediately rinsed		43.46°	±0.00°
		Average		43.46°	

IV. The Influence of the Size and Shape of the Vessel in which the Freezing Point is Determined.—To ascertain what influence is exerted by the use of a narrower test-tube than prescribed, the freezing-point of two fatty acids was determined in a tube only two and one-half cm. in diameter, as well as in one of the usual diameter, three and one-half cm., with the following results:

	Freezing-point obtained in the wide tube.	in the narrow tube.	Difference.
Fatty acid I.....	43.52°	43.34°	0.18°
Fatty acid II....	42.88°	42.65°	0.23°
Average.....			0.20°

These results by no means fix the allowable minimum diameter of the tube, as, *a priori*, the possibility is not excluded of obtaining a still higher freezing-point by the use of a tube of still greater diameter.

Accordingly, the freezing-point of the same fatty acid was determined, first, in a test-tube of the usual diameter, three and one-half cm., and then in a similarly shaped vessel having a diameter of seven cm., making about four times as much fatty acid around the thermometer in the second case as in the first. The freezing-points obtained were as follows:

In tube three and one-half cm. in diameter..... 43.45°
" " seven cm. in diameter 43.46°

which show that the diameter of the tube may be increased from three and one-half cm. without disturbing the ratio between the amount of heat radiating from the fatty acid through the walls of the tube and the amount of liberated latent heat.

Consequently a tube three and one-half cm. or more in diameter answers perfectly for the correct determination of the freez-

ing-point, but it is not permissible to use one appreciably narrower than this.

V. The Influence of the Length of the Thermometer.—In order to demonstrate and also to estimate the error (a too low result) caused by an incomplete immersion of the thermometer in the liquid, thus allowing a portion of the column of mercury to project above its surface, the shortened thermometer recommended above, and a long (normal) one were first tested by a complete immersion in a water-bath, when each registered exactly the same temperature (43°); after which they were simultaneously placed in the test-tube containing water at 43°. The shortened thermometer was immersed to the 35° mark, leaving but 8° of mercury above the surface of the water, while the long thermometer could be immersed to only its zero mark, leaving fully 43° of mercury exposed. The whole was then placed in an air-bath, kept at a temperature of 20° in order to avoid the error of radiation. The reading of the long thermometer was about 0.13° below that of the shorter one.

This error was now calculated for each thermometer, giving, theoretically, for the long

thermometer	0.15°
while for the shorter one, only	0.03°
the difference of	0.12°

being the theoretical error introduced by using a long (normal) thermometer, and agreeing closely with the experimental determination of the error (0.13°).

Though, of course, this error is not completely eliminated by using a shortened thermometer, still it is so reduced as to be of no practical importance.

RECENT WORK ON THE SUGARS.

By B. B. Ross.

(*Continued from page 553.*)

Received May 14, 1894.

DETERMINATION OF WATER IN SUGARS.

Herzfeld (*Ztschr. des Ver. f Rübenzucker*, **43**, 130, *Bull. Assoc. Chim. Belg.*, **6**, 267) reports the results of a large number of experiments in the determination of the amount of water in

syrups and sugars, the drying being effected both in air and in vacuo.

The drying in contact with air was conducted at a temperature of about 105° C., the samples under examination being contained in nickel dishes about eight cm. in diameter and two cm. deep.

For syrups, three grams of material were employed, along with thirty grams of well-purified quartz sand.

In the water determinations in vacuo, a temperature of about 107° C. was employed, while in the experiments with Soxhlet's drying apparatus, the operation was conducted at about 103°–104° C.

A syrup prepared by dissolving a definite weight of sugar in a known weight of water was used in a large number of the tests made.

After three hours drying in vacuo, the results secured closely approximated the theoretical figures, and at the end of five hours' drying the correspondence was almost exact.

In drying in air, eight hours were required to obtain results agreeing with the theoretical water content, and the loss in weight still continued, even after fifty-six hours' drying.

In the estimation of water in syrups, to which alkaline salts had been added, it was likewise found that concordant results could be most quickly secured in vacuo.

With raw sugars, as well as with syrups, the results by drying in air were quite appreciably higher than those secured in vacuo, especially where the drying was at all protracted.

For maintaining a temperature of approximately 105° C., the author employs toluene between the walls of the drying apparatus.

Josse (*Bull. Assoc. Chim. France*, **10**, 656) proposes to employ in the determination of water in syrups and masse cuite, a dried and weighed spiral of filter paper which is to be saturated with the sample under examination.

A strip of filter paper, one to two cm. wide and about three meters in length, is coiled into a spiral form, placed in a capsule about seven cm. wide and two cm. deep, dried and weighed.

Two grams of syrup or masse cuite is next brought into the dish, about six to eight cc. of water added, and after the mixture has been warmed slightly the paper spiral is inserted.

The liquid is readily absorbed by the filter paper, and the drying is conducted at 100°–110° C., until a constant weight is secured, about two hours being ordinarily required to complete the operation.

It is claimed that the method is accurate as well as rapid.

DETERMINATION OF ASH IN SUGARS.

Courtonne (*Bull. Assoc. Chim. France*, **10**, 223) describes in detail the method proposed by him for the determination of ash in sugars by ignition of the sample in the presence of ferric oxide. The process is conducted as follows:

Place in a platinum capsule two grams of freshly calcined ferric oxide, which should also have been thoroughly washed to insure freedom from sulphuric acid. Into the same vessel weigh five grams of sugar, or about two grams of molasses. After addition of a little water to the mass, the mixture is evaporated rapidly upon a sand-bath or a metallic plate and heated over a Bunsen burner until frothing takes place. The capsule is now placed in a muffle heated scarcely to dull redness; the combustion is found to take place quite rapidly, and the incineration is sometimes completed in a quarter of an hour—always within half an hour.

Among the advantages presented by this process, it is claimed that, as in the Alberti and Hempel method, where quartz sand is employed, the mass is well divided by the admixture with the ferric oxide, and the points of contact of the material with the air are thus multiplied. The formation of carbonates is also prevented and the ferric oxide facilitates oxidation by acting as a carrier of oxygen from the air to the sample; further, the low temperature employed prevents the loss of volatile salts, such as chlorides, while the rapidity of execution of the incineration is an important advantage.

This method should also have the preference over the quartz sand process for the reason that the platinum vessels used are much less readily attacked where ferric oxide is employed.

Vivien (*Bull. Assoc. Chim.*, **10**, 225) reports the result of experiments with Courtonne's method, employing different temperatures and different periods of time for the ignitions.

The results were found to be always lower than those secured

by the sulphuric acid method and the direct ignition process, the figures for the same sample not being at all concordant.

A constant weight was not obtainable by this process and the composition of the ash varied considerably with the length of time of the incineration and the temperature employed.

At somewhat elevated temperatures it was found that chlorides were more or less attacked and, possibly, partly volatilized.

ALBERTI AND HEMPEL'S METHOD FOR ASH DETERMINATIONS.

Stift (*Oest. Ztschr. Zucker*, **22**, 22; *Chem. Ztg. Rep.*, **17**, 102), as the result of a large number of experiments with different sugar products, concludes that this method, by proper and careful execution, and with previous thorough testing of the quartz sand employed, is to be most highly commended, yielding, as it does, concordant results and, in contrast to other methods, furnishing more correct and uniform figures for the content of inorganic substances.

A point of great importance in the performance of the incineration is the necessity of the employment of quartz sand of absolute and known purity.

With sugars containing considerable proportions of nitrates (which are decomposed in this process), it is necessary to make a separate estimation of nitric acid.

THE DETERMINATION OF VOLATILE AND INSOLUBLE FATTY ACIDS IN BUTTER FAT.

By W. H. Beal.

Received July 27, 1894.

A FEW years ago when called upon to make examinations of the fat in a number of samples of cream the author attempted to use for that purpose the then recently proposed method of Waller as modified by Moore[1] which is briefly as follows: Two and five-tenths grams of fat are placed in a weighed Erlenmeyer flask and saponified with one gram of potassium hydroxide dissolved in fifty cc. of seventy per cent. alcohol. After heating until saponification is complete the alcohol is driven off in a boiling water-bath. The resulting soap is dissolved in fifty cc.

[1] See *J. Am. Chem. Soc.*, 11, 144, *1889*.

of water and decomposed by means of twenty cc. of dilute sulphuric acid (one part of strong acid to ten parts of water). The flask is connected with a condenser and fifty cc. are distilled off, the distillate passing through a small filter in the mouth of the receiving flask. The distillate is titrated with one-tenth normal sodium hydroxide solution, using phenolphthalein as an indicator. Fifty cc. of water are added to the contents of the flask and an equal quantity distilled off and titrated as before. This treatment is repeated until only one-tenth cc. or less of soda solution is required to neutralize the distillate. After cooling, the liquid remaining in the flask is poured off from the solidified insoluble acids through the same filter used for the distillates. The insoluble acids are repeatedly washed with hot water until all traces of sulphuric acids are removed. The condenser is then washed out with hot alcohol and the filter exhausted with the same solvent, the washings being collected in the flask containing the insoluble acids. The alcohol is driven off and the flask and contents dried at 100° C. and weighed.

With proper precautions satisfactory results were obtained with this method, but the work had not proceeded far before grounds for the following objections became evident: (1) Saponification is slow and removal of the last traces of alcohol in the dilute solution recommended is difficult; (2) there is danger from violent bumping, which it was found impossible to entirely prevent; (3) there is danger of charring the fat adhering to the sides of the flask when the contents of the latter are reduced to a small bulk, causing the final insoluble acid to have a brownish color instead of a pale yellow color which is normal; and (4) inconvenience and loss of time is occasioned by the necessity of frequently replenishing the contents of the flask.

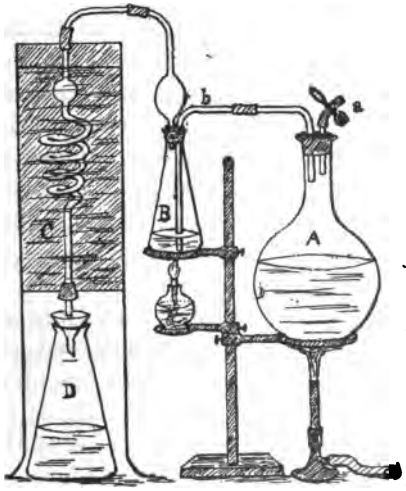
An attempt to devise a process which would in a measure, at least, overcome these difficulties, which it may be observed are in large part shared by all the methods now in vogue, resulted finally in the adoption of the following method of procedure:

Volatile Acids.—Two and eight-tenths to two and nine-tenths cc. (approximately two and five-tenths grams) of the pure fat were measured by means of a narrow pipette into a weighed Erlenmeyer flask (long narrow form preferable) of 200 cc.

capacity. Saponification was accomplished by adding two cc. of a solution prepared by dissolving fifty grams of potassium hydroxide (free from carbonates) in 100 cc. of water and five cc. of strong (ninety-five per cent.) alcohol. The flask was connected with a reflux condenser and heated on a water or steam-bath until saponification was complete. Five minutes was usually amply sufficient for this purpose. The last traces of alcohol were quickly and completely removed with the filter pump by means of a device described by L. F. Nilson.[1]

The soap thus obtained was dissolved in thirty cc. of warm water and decomposed with twenty cc. of a twenty per cent. solution of orthophosphoric acid. The volatile acids were expelled from the flask by means of a current of steam, using the apparatus described below. The operation was usually considered complete when 500 cc. had passed over, although, as an extra precaution, fifty cc. more was distilled over and titrated separately. For titration, decinormal soda solution and phenolphthalein were used.

The apparatus used in distilling is shown in the accompanying cut. A is a liter flask two-thirds full of water, which is kept boiling. The steam generated is forced into the decomposed soap solution in B through the tube b, which reaches nearly to the bottom of the flask. This second flask is provided with a small lamp, so regulated as to prevent increase, by condensation, of the solution in the flask, and finally to bring its contents to a small bulk (about fifteen cc.). The condenser C consists of a copper tank, fifteen inches high, twenty inches long, and five inches wide, having four perforations in the bottom, into which glass spirals are fitted by means of rubber stoppers, and provided with proper inlet and



[1] *Ztschr. anal. Chem.*, 28, 176.

overflow pipes for the water supply. Provision was thus made for four distillations at one time. The distillates were collected in wide-mouthed Erlenmeyer flasks, marked on the neck at 500 cc., and carrying funnels with small filters, through which the distillates passed.

Insoluble Acid.—After the distillation was completed, the condenser and connections were rinsed back with boiling water into the flask containing the non-volatile acids. The latter were shaken up with the hot water, and the solution, when cold, was passed through the same filter used for the distillate. Hot water (about 100 cc.) was again added, shaken up with the contents of the flask, and when cold filtered off as before. This operation was repeated until the washings contained no trace of phosphoric acid. The filter was then exhausted with hot, strong alcohol, and the solution allowed to run into the flask containing the insoluble acids. The alcohol was driven off on the water-bath and the fatty acids dried at 100° C. in the air-bath until they began to gain weight.

Very uniform and concordant results were obtained by this method in the examination of a large number of samples of butter fat.

The expulsion of the volatile acids by means of a current of steam, which it was afterwards found[1] had already been suggested by Goldman,[2] proved to be a decided improvement over direct boiling of the solution containing the fatty acids. When the operation had been started it required but little further attention and there was no danger of bumping or of overheating the insoluble acids. The volatile acids were very thoroughly removed, the last distillate of fifty cc. never requiring more than two-tenths cc. of soda solution for neutralization.

The first fifty cc. of distillate obtained by this method required less soda solution than that obtained by the Reichert or the Moore-Waller methods, and titration of each successive fifty cc. of the total 550 showed that expulsion of the volatile acids was much more gradual and uniform than in the latter methods.

[1] *Analyst, Sept. 1892*, 174.

[2] *Chem. Ztg.*, *1888*, 12, 183; 14, 216; and 20, 317.

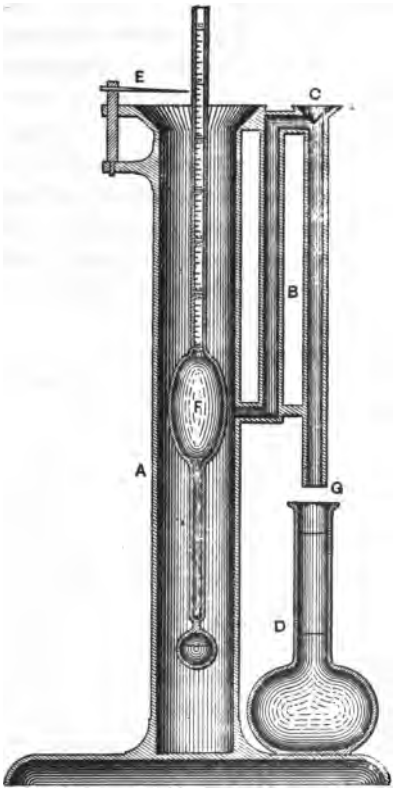
A GRAVIMETER FOR SUGAR ANALYSIS.[1]

By W. K. Gird.

Received June 28, 1894.

FOLLOWING is a description of the construction and operation of this apparatus; the drawing showing the instrument and appurtenances in section:

A represents the main tube to hold the solution under treatment; B, overflow pipe; C, air vent to prevent siphonage, constructed in funnel form to facilitate cleaning; D, the usual graduated flask; E is an index finger pointing to the saccharometer, constructed so as to swing out of the way when necessary, and to stand for convenience of reading, say five graduations above the surface of the fluid; F, hydrometer or saccharometer, weighing exactly 26.048 grams; G, point of discharge into the flask D.



Although the operation is manifest, a few explanatory words may be appropriate.

The operator closes aperture G with his finger, then fills the main tube with the solution until it shows full at C, then strike off foam from the top of the main tube, remove the finger from G and permit the excess to escape to the last drop which must be removed.

This will leave the tube B moistened with the fluid under analysis, so that the condition will be left precisely the same as it will be after the delivery of the discharge hereafter explained,

[1] Read before the Midwinter Fair Congress of Chemists at San Francisco, June 8, 1894.

so that there can be no loss nor no gain either in quantity or quality. Next, place flask D under the overflow G and insert the saccharometer in the usual manner bring up the mouth of the flask so as to catch the last drop. The fluid in the flask will then be the required quantity. Now, bring the point E to the index on the saccharometer and note the reading for Brix, to which add five, representing the height of the finger above the surface.

This instrument is constructed upon the sole principle of displacement determined by the weight of the saccharometer which displacement is always the same, not being affected by difference of temperature, rendering the use of the thermometer and corresponding tables unnecessary.

In taking the Brix as described above, the precise weight is conveyed into flask D through the overflow, thus dispensing entirely with use of the pipette and weighing as in the old system.

The results are absolute, doing away with all liability to error, inasmuch as no readings are necessary and all the manipulations are regulated and controlled by easily observed limitations.

In making many analyses as for instance in the laboratory at Chino numbering perhaps 200 per day, the advantages derived from the use of this instrument both in rapidity and accuracy can scarcely be estimated.

NOTE.—This instrument has since been improved, notably in the addition of a permanently attached thermometer, which, in addition to the usual thermal graduations, has also a table on its face for the corrections due to differences of temperature.

ON THE QUALITY OF POTASSIUM IODIDE, SOLD IN THE MARKET AS U. S. P.[1]

BY CHAS. O. CURTMAN.

Received August 4, 1894.

SIXTEEN samples were procured for examination by purchasing original packages made by twelve different firms. For six of them I am indebted to the courtesy of a friend, who bought them for a similar purpose and divided with me. To these, the tests of purity directed by the U. S. P. were applied seriatim, with the following results:

A. No residue should be left when one gram of the salt is dissolved in two cc. of diluted alcohol of sp. gr. 0.928. To this test fourteen specimens conformed; two left a small residue (Nos. 5 and 9).

[1] No. 5. Report Research Committee B.

B. To the test for excess of alkalinity the same fourteen specimens conformed, while two exceeded the limit (Nos. 5 and 9).

C. In the same two specimens and two others (5, 8, 9, 11), the flame test showed a considerable amount of sodium, while in the others the violet potassium flame appeared at once.

D. In both of these specimens (5 and 9) iodate was found (about 0.8 per cent.) while the others were free from it. (Nos. 5 and 9 were from the same firm.)

E. The hydrogen sulphide test showed the absence of metallic impurities in all of the sixteen specimens.

F. The barium chloride test indicated sulphate in five specimens (3, 5, 8, 13, 15); the others were free from it.

G. A small trace of nitrate was found, by reduction to ammonia, in three specimens (4, 7, 14); a somewhat larger amount in three others (3, 8, 13).

H. No iron could be detected in any of the specimens by potassium ferrocyanide.

I. Cyanide was absent in all specimens.

K. Titration with decinormal silver nitrate using potassium chromate as indicator, yielded with one gram each of the well-dried specimens as follows:

cc. of $\frac{N}{10}$ $AgNO_3$ required for one gram of specimen.	Per cent. of KI.	No. of specimens.
60.25	100.00	1, 10, 12
60.30	99.40	2
60.50	99.67	15
60.55	99.60	6
60.63	99.50	4, 7, 8, 11, 14

Making eleven specimens which conformed to the U. S. P. standard of at least 99.50 per cent.

60.70	99.40	5, 9
60.75	99.33	3
60.80	99.30	16
60.85	99.20	13

Making five specimens below standard.

(The second decimal of a cubic centimeter was estimated on graduation into one-twentieth cc., where it fell between 0.00 and 0.05). Bromide could not be detected in any of the specimens.

Chloride was found in eight specimens (Nos. 3, 4, 5, 7, 13, 14, 15, 16), by precipitating with a slight excess of silver nitrate, washing thoroughly, and digesting for about twenty-five

minutes in a five per cent. solution of ammonium carbonate (free from hydroxide). The filtered liquid became turbid on acidulation with nitric acid.

Mohr's method of titration with decinormal silver nitrate, using potassium chromate as indicator, gives direct results when bromide and chloride are absent and the impurity consists of substances which do not precipitate silver nitrate. But when chloride is present (bromide is very rarely found in potassium iodide), its smaller molecular weight will require the use of a greater volume of silver solution than would suffice for pure iodide, and a calculation becomes necessary to obtain correct values. This may be avoided by reference to the following table, which, for potassium iodide containing chloride as only impurity, gives the percentage of pure potassium iodide corresponding to the number of cubic centimeters of decinormal silver nitrate used for one gram of specimen.

cc. $\frac{N}{10}$ $AgNO_3$.	Per cent. of KI.	cc. $\frac{N}{10}$ $AgNO_3$.	Per cent. of KI.	cc. $\frac{N}{10}$ $AgNO_3$.	Per cent. of KI.
60.2555	100.000	62.8	96.571	65.4	93.068
60.3	99.940	62.9	96.437	65.5	92.933
60.4	99.805	63.0	96.302	65.6	92.799
60.5	99.670	63.1	96.167	65.7	92.664
60.6	99.536	63.2	96.033	65.8	92.529
60.7	99.401	63.3	95.898	65.9	92.395
60.8	99.266	63.4	95.763	66.0	92.260
60.9	99.132	63.5	95.628	66.1	92.125
61.0	98.997	63.6	95.494	66.2	91.990
61.1	98.862	63.7	95.359	66.3	91.856
61.2	98.727	63.8	95.224	66.4	91.721
61.3	98.593	63.9	95.089	66.5	91.586
61.4	98.458	64.0	94.955	66.6	91.451
61.5	98.323	64.1	94.820	66.7	91.317
61.6	98.188	64.2	94.685	66.8	91.182
61.7	98.054	64.3	94.550	66.9	91.047
61.8	97.919	64.4	94.416	67.0	90.912
61.9	97.784	64.5	94.281	67.1	90.778
62.0	97.649	64.6	94.146	67.2	90.643
62.1	97.515	64.7	94.011	67.3	90.508
62.2	97.380	64.8	93.877	67.4	90.373
62.3	97.245	64.9	93.742	67.5	90.239
62.4	97.110	65.0	93.607	67.6	90.104
62.5	96.976	65.1	93.472	67.7	89.969
62.6	96.841	65.2	93.338	67.8	89.834
62.7	96.706	65.3	93.203	67.9	89.700

To avoid the error occasioned by potassium chloride, I repeated

some of the titrations with decinormal silver nitrate, using starch iodide as indicator (Pisani's method). A gravimetric method had been devised in 1872 at Goettingen, by Hübner, Spezia and Frerichs, in which thallous chloride was used as precipitant of iodides, and I concluded to convert this into a simple volumetric process and apply it to the present investigation. Thallous chloride, TlCl = 239.07, at 15° C., requires 360 parts of water for solution (100 cc. of water dissolve 0.2777 gram of thallous chloride). A centinormal solution requires 2.3907 grams of TlCl for one liter. Thallous iodide, TlI = 330.23, at 15° C. requires nearly 12,000 parts of pure water for solution, and about 16,000 parts if potassium chloride be present or still more if the water be acidulated with acetic acid. Thallous bromide is much more soluble than the iodide, and its solution precipitates iodide promptly.

After a trial of various substances as indicators of the final point, spotting with sodium palladious chloride was found to yield very accurate results. The titration was conducted as follows: 0.16556 gram of potassium iodide (ten cc. of a solution, containing 1.6556 grams in 100 cc.) were placed into a capacious flask and centinormal thallous chloride added until spotting showed the disappearance of iodide from the solution.

For spotting, a ten per cent. solution of sodium palladious chloride was, by means of a pipette drawn into a broad line (two mm.) upon a plate of milk glass (photographers opal) and permitted to dry. As soon as it became doubtful whether further addition of thallous chloride produced a precipitate, a drop of liquid was taken out of the flask with a glass rod and drawn across the line of palladious chloride upon the plate. As long as iodide was present a dark spot formed at the crossing, and the number of cubic centimeters used was marked at its end in pencil. At the opposite end of the palladium line a drop of a saturated solution of thallous iodide was placed, so as to serve with its faint color for comparison with the drops taken from the flask. To guard against deception the same specimen was repeatedly tested by different operators, but the indications corresponded sharply.

The following results were obtained, with the first six numbers

of the specimens by the three methods: Mohr's with silver nitrate and potassium chromate (one gram of the specimen being used and the percentage corresponding to the cubic centimeters inserted from the table). Pisani's method with silver nitrate and starch iodide (1.6556 grams being used and each cubic centimeter of $\frac{N}{10}$ $AgNO_3$ deemed equivalent to one per cent. of KI) and with the thallous chloride, (0.16556 gram being used and one cc. counted as one per cent.).

No. of specimen.	Mohr's method. cc. used.	Mohr's method. Per cent. KI.	Pisani's method. Per cent. KI.	Thallous chloride. Per cent. KI.
1	60.25	100.00	100.00	100.00
2	60.30	99.94	99.94	99.94
3	60.75	99.33	99.20	99.20
4	60.60	99.54	99.40	99.35
5	60.70	99.40	99.30	99.30
6	60.55	99.60	99.55	99.55

The method of Pisani and that with thallous chloride yielded somewhat less percentages with some of the specimens than Mohr's method, but gave, in almost every instance, results equal to each other.

SAINT LOUIS, MO., July 22, 1894.

SEWAGE DISPOSAL AT WORCESTER, MASS.

BY HARRISON P. EDDY.

Received February 6, 1894.

SINCE the description of the sewage disposal works at Worcester, by Dr. Leonard P. Kinnicutt, in 1891, (See *J. Anal. Appl. Chem.*, **5**, 544), many important changes have been made both in the methods employed and machinery used. The capacity of the plant has also been greatly increased. The amount of water then dealt with was 3,000,000 gallons per twenty-four hours, while now between 10,000,000 and 15,000,000 gallons are successfully treated in the same time.[1]

Before examining in detail the work accomplished it may be well to look briefly into the history connected with the purification of sewage at Worcester, that the problems encountered may be more fully understood.

For many years the city turned her sewage directly into the Blackstone river, a stream of about 23,000,000 gallons during

[1] Descriptions of this plant showing the engineering details are given in the *Engineering News* for January 11 and 18 and the *Engineering Record* for January 13, to which the reader is referred.

the summer months. This stream is fed, in part, by water from the northern water shed which tributary is called Millbrook, and it flows through the center of the city. This water amounts to about 8,000,000 gallons per day during the summer months. Millbrook being so conveniently situated was made the trunk sewer and to-day all the sewage of Worcester is discharged into it. For a number of years there was so little filth turned into the stream that the villages situated near the river, below the city, had little cause for complaint, but with the increase of population the river became very foul until, in 1886, the complaint from neighboring villages was heeded by the Massachusetts Legislature, and the right, granted in 1867, to turn sewage into the Blackstone river was revoked. An act was passed June 25, 1886, compelling Worcester to "remove from its sewage, before it is discharged into the Blackstone river, the offensive and polluting properties and substances therein, so that, after its discharge into said river * * * it shall not create a nuisance or endanger the public health." Four years were given the city in which to perfect some system for the accomplishment of this result, and accordingly, City Engineer Chas. A. Allen personally inspected works at home and abroad and after a careful study of the local problems recommended that a plant, capable of dealing with 4,500,000 gallons of sewage daily, be constructed and that the method of treatment employed be that of chemical precipitation.

This plant was first operated June 25, 1890, from which time until July, 1893, about 3,000,000 gallons of sewage were treated daily, except in time of storm when the entire flow was turned directly into the stream. It was found from the experiments of these three years that, by chemical precipitation, the sewage could be purified to an extent which would admit of its being turned into the river. Having settled this point, the next problem confronting the city was the treatment of the entire amount of sewage, as thus far only about twenty per cent. had been taken to the purification works. The actual amount of sewage is between 5,000,000 and 8,000,000 gallons per day, while the water from the brook, mentioned above, increases this to 10,000,000 or 15,000,000 gallons in dry weather, while in storm this amount is so largely increased that its treatment is wholly out

of question. The city is almost wholly sewered on the combined plan. From the start the plan had been to separate the waters of Millbrook from the sewage, thus leaving only a moderate amount of water with which to deal. On further consideration, however, it seemed advisable, for the present at least, to take as much of the sewage to the plant as possible. Accordingly, the present city engineer, then superintendent of the sewer department, Mr. F. A. McClure, proposed that ten additional settling basins, with the other necessary appliances, be provided, and that the whole, or as much as possible of the present flow be taken the to works. This plan having been adopted, work was begun in 1892 and the enlarged plant put in operation about the middle of July, 1893, since which time the entire flow has been treated.

The new basins differ somewhat from the old ones, being 166⅔ feet long and forty feet wide; the capacity is, however, the same, as are also the general features of construction. The effluent instead of returning to the steps provided in the old plant, is utilized to furnish power for pumping sludge during the day and for running a dynamo at night. A Shone ejector has been provided for pumping the sludge from the new work and part of that from the old. This ejector has proved to be very efficient and is much better adapted to use with sludge than the submerged centrifugal pumps employed on the original plant, as there is not the danger of clogging. It is run by air furnished by a compressor, power for which is derived from the water-wheel. Thus expense of steam is avoided.

The agitators originally used for mixing the chemicals have been taken out and two new tanks substituted; these are built of quarter-inch boiler steel and are set in masonry. These tanks are each sixteen feet long, eight feet wide, and three feet two inches deep. The bottom is fluted and through each of three valleys runs an iron pipe perforated with quarter-inch holes about fifteen inches apart. These pipes are connected by means of a main, four-inch pipe to an air receiver. Through the holes in these pipes air is blown at a pressure of sixty pounds, although so high pressure is not absolutely necessary and even air taken directly from the compressor has worked satisfactorily. This air agitates the liquid giving it the appearance of boiling.

The lime is thus thoroughly mixed with the water in the tank and runs from it in the form of milk of lime. The old practice of grinding the lime has been abandoned, it having been found that slaking in water was just as efficient and that a more economical use obtained by this thorough water-slaking before coming in contact with the sewage. By these changes a considerable saving in power used has resulted and, by the more thorough slaking of the lime, the amount required has been reduced about thirty per cent.

The treatment originally adopted as recommended by Engineer Allen, consisted in the addition to the sewage of lime and alumihum sulphate. It has been found, however, that the alumina need not be used, on account of the large quantities of iron sulphate contained in the sewage. This iron sulphate is not evenly distributed through the sewage of the day but comes at stated periods. At night, when the sewage is comparatively weak, that containing the copperas is stored crude in one or two of the settling basins and is used during the day, when there is a scarcity of iron and when otherwise aluminum sulphate should be added. By utilizing this iron sulphate, considerable expense is avoided and a perfectly clear, odorless effluent obtained. Lime alone is now added to the sewage, about 900 pounds being required for each million gallons. The highest grade obtainable is used, as it proves most economical in the end. The chemicals formerly entered the sewage just above the salmon ladder but have since been carried about 200 feet up the sewer, that a more thorough mixture might be obtained.

The chemical precipitation of sewage has been practiced in England for more than twenty-five years and yet, the published results of experiments performed there are so meager as to be practically of no assistance here. Consequently when this method was adopted in Worcester great faith had to be placed in future developments. From the first day the plant was operated, continued experiments have been made; at first these were wholly mechanical and random but it was soon found that a systematic study of the whole problem must be made if the work was to be successful. Accordingly the problems met in actual manipulation are made subjects of special investigation

in the well-equipped laboratories. That this move has been productive of good is shown by the reduction of nearly fifty per cent. in the cost of treatment, so far as effected by the chemicals used. Analyses of sewage and effluent are made daily. The samples for analysis are each composed of twenty-four portions taken hourly. Thus by averaging results for several days a mean is obtained, so that comparisons may be made with a certainty that the effluents correspond to the sewages. The percentage of impurity removed from the sewage is readily calculated and is indicative of the efficiency of the plant. Records of the analyses are kept in two forms: one is simply the numerical tabulation, the other a graphic illustration showing at a glance the result of treatment over any period of time. It will be noticed, from accompanying Table A, that the sewage dealt with is remarkably strong, considering that about half of it is water coming directly from North Pond. It is also interesting to note that the effluent contains only two and one-half parts per 100,000 parts matter in suspension and that of this only one and one-tenths parts are organic matter. Thus by treatment the organic suspended matter has been removed to the extent of 90.76 per cent. The total dissolved residue and the total and dissolved fixed residue are negative results, undoubtedly due to the large quantity of lime retained in solution in the effluent. From Table A the result of treatment of sewage since July can be followed by months, and the averages are given for the whole period. The work done as shown by the results of these analyses is very good and should fully carry out the object of the plant; *viz.*, not to transform sewage into a potable water, but to abate and finally terminate a nuisance to neighboring villages along the Blackstone river. During the last three years the sludge has been disposed of in various ways and numerous experiments have been performed and are now being carried on, which for lack of space cannot be described at this time. It may be added that the aim has been to make the plant attractive to the eye by the architecture of the new buildings, the lighting system and the grading around the basins, that the visitor may have his preconceived, erroneous impression of disagreeable sights and odors dispelled.

TABLE A.

Date of Collection.	Residue on evaporation.									Ammonia.				Oxygen Consumed.		Chlorine.
	Total residue.			Volatile residue.			Fixed residue.			Free.	Albuminoid.			Unfiltered.	Filtered.	
	Total.	Dissolved.	Suspended.	Total.	Dissolved.	Suspended.	Total.	Dissolved.	Suspended.		Total.	Dissolved.	Suspended.			
Sewage, July 19-31, 1893	70.2	48.0	22.2	32.1	17.9	14.2	38.1	30.1	8.0	1.043	0.622	0.403	0.219	5.62	3.18	6.64
Effluent, " " "	59.2	56.0	3.2	16.0	13.5	2.5	43.2	42.5	0.7	0.973	0.356	0.239	0.069	3.29	2.56	6.44
Parts removed	11.0	— 8.0	19.0	16.1	4.4	11.7	— 5.1	—12.4	7.3	0.073	0.266	0.164	0.231	2.33	0.62	0.2
Per cent. "	15.67	—16.67	85.59	50.16	24.59	82.39	13.39	—41.20	91.23	6.71	42.78	40.69	46.58	41.47	19.5	2.99
Sewage, Aug., 1893	61.2	40.9	20.3	30.7	18.6	12.1	30.5	22.3	8.2	1.137	0.558	0.258	0.300	5.9	3.24	6.49
Effluent, " "	53.9	50.7	3.2	14.9	13.5	1.4	39.0	37.2	1.8	1.083	0.333	0.264	0.069	3.7	3.42	6.49
Parts removed	7.3	— 9.8	17.1	15.8	5.1	10.7	— 8.5	—14.9	6.4	0.054	0.225	—0.06	0.231	2.2	— 0.18	0.00
Per cent. "	11.92	—19.33	84.24	51.47	27.42	88.43	27.87	66.82	78.05	4.75	40.33	—2.32	77.00	37.28	— 5.56	0.00
Sewage, Sept., 1893	62.1	43.4	18.7	29.3	17.0	12.3	32.8	26.4	6.4	1.488	0.522	0.247	0.275	5.11	3.15	6.16
Effluent, " "	54.0	51.7	2.3	14.6	13.5	1.1	39.4	38.2	1.2	1.426	0.25	0.204	0.046	3.33	3.03	6.01
Parts removed	8.1	— 8.3	16.4	14.7	3.5	11.2	— 6.6	—11.8	5.2	0.062	0.272	0.043	0.229	1.78	0.12	0.15
Per cent. "	13.04	—19.13	87.70	50.17	20.59	91.05	—20.12	—44.70	81.25	4.17	52.11	17.42	83.28	34.83	3.81	2.43
Sewage, Oct., 1893	67.7	46.4	21.3	28.7	16.6	12.1	39.0	29.8	9.2	1.584	0.576	0.279	0.297	4.96	2.69	5.57
Effluent, " "	54.0	51.6	2.4	13.3	12.5	0.8	40.7	39.1	1.6	1.504	0.288	0.214	0.074	3.37	3.13	5.31
Parts removed	13.7	— 5.2	18.9	15.4	4.1	11.3	— 1.7	— 9.3	7.6	0.08	0.288	0.065	0.223	1.59	— 0.44	— 0.74
Per cent. "	20.21	—11.20	88.74	53.65	24.70	93.40	— 4.36	—31.21	82.60	5.05	50.00	33.3	75.08	32.06	—16.36	—13.3
Sewage, Nov., 1893	57.5	41.7	15.8	22.8	13.1	9.7	34.6	28.6	6.0	1.548	0.45	0.22	0.23	4.49	2.14	5.69
Effluent, " "	51.4	50.0	1.4	12.1	11.5	0.6	39.3	38.5	0.8	1.465	0.196	0.155	0.041	3.49	3.30	5.97
Parts removed	6.1	— 8.3	14.4	10.7	1.6	9.1	— 4.7	— 9.9	5.2	0.83	0.254	0.065	0.189	1.00	— 1.16	— 0.28
Per cent. "	10.69	—19.91	91.11	46.93	12.21	93.80	—13.58	—34.61	86.67	5.36	56.44	29.54	82.19	22.27	—54.2	— 4.92
Av. of sewage analysis, July 19 to Dec. 1, 1893	62.8	43.5	19.3	28.3	16.5	11.8	34.5	27.0	7.5	1.395	0.536	0.266	0.27	5.17	2.85	6.05
" Effluent " " " " "	53.9	51.5	2.4	13.9	12.8	1.1	40.0	38.7	1.3	1.325	0.276	0.213	0.063	3.43	3.15	6.23
Parts removed	8.9	— 8.0	16.9	14.4	3.7	10.7	— 5.5	—11.7	6.2	0.070	0.26	0.053	0.207	1.74	— 0.3	— 0.18
Per cent. "	14.18	—18.40	87.56	50.88	22.43	90.67	15.94	—43.33	82.6	5.010	48.49	19.88	76.67	33.65	—10.53	— 2.98

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. IV.]

OIL-GAS.[1]

BY W. A. NOYES, W. M. BLINKS AND A. V. H. MORY.[2]

SOME years ago Armstrong and Miller[3] made a study of the gas made from petroleum by subjecting it to a high temperature, and of the oil deposited on condensing the gas. The following study of the gas made from petroleum by a somewhat different process and which gives in some respects different results may be of interest.

In the Pintsch system[4] as described by Armstrong and Miller two D shaped retorts of cast iron are set one above the other, the largest size in use being six feet four inches long, ten inches wide and nine and three-fourths inches deep. The retorts are heated to a bright cherry-red and the oil may be run into the upper retort at the rate of about twelve and one-half gallons per hour. About eighty feet of gas per gallon of oil is considered a good yield.

By the Citizens Fuel and Gas Company of Terre Haute, gas is made from petroleum in large generators, one having a capacity of about 450 cubic feet of gas per minute, and two smaller ones with a capacity of 250 feet per minute, during the generation of the gas. The larger generator consists of an outer cylindrical shell of three-eighths-inch boiler steel, twenty feet high by eight feet in diameter, lined with fire-brick to a thickness of sixteen inches. The interior is composed of alternate chambers and checker-work compartments of fire-brick. Starting at the bottom there is an open chamber to the height of two and one-half feet, then, resting upon six twelve-inch arches, the checker-work of brick is built up, rows of brick, touching end to end and two and one-half inches apart, extending from wall to wall, composing the first tier, then upon these other rows are laid at

[1] Read at the Brooklyn meeting, August 15, 1894.

[2] The work described in this paper formed the basis of a thesis presented to the Faculty of the Rose Polytechnic Institute by Mr. W. M. Blinks and Mr. A. V. H. Mory for the degree of Bachelor of Science.

[3] *J. Chem. Soc.*, (London) 49, 74, (1886).

[4] *J. Soc. Chem. Ind.*, *1884*, 463. We are indebted to Mr. W. B. Landon of Lafayette College for this statement, as the Journal is not accessible to us.

right angles to the first, then the next tier so as to be directly over the open squares formed by the first two rows, and so on, making the checkerwork to the height of five and one-half feet. The bricks are laid in, one upon another, without mortar or fire-clay

Above this checkerwork is a chamber three feet high, then arches and more checkerwork for five and one-half feet and then another chamber extending to the top. A heavy iron door fourteen inches in diameter is provided at the top. By opening and shutting this it is made to act as a regulator for equalizing pressures when reversing operations. For heating the generator, oil is injected into the top and middle chambers by means of a steam-jet, air being admitted at the same points through five-inch valves. For generating gas, oil is injected into the top chamber through three jets. The gas which is formed leaves the chamber at the bottom through a sixteen-inch pipe lined with fire-brick and leading into the water-seal. The gas as it leaves the generator is too rich for burning in ordinary burners, hence in the seal-box it is diluted with ordinary air injected by steam through a four-inch pipe into the top of the seal. In the process as formerly used this air was injected into the generator with the oil and the oxygen which it contained appeared as carbon dioxide and carbon monoxide in the gas produced. This form of the process is still in use elsewhere.

The seal-box is three and one-half feet in height by four feet in diameter and the pipe leading from the generator dips eight inches below the water surface. A stream of cold water runs continuously into the seal-box, condensing the tar which is carried with the overflow water into the tar well. From the seal the gas passes through a tower scrubber twenty feet in height where it is washed with cold water, then through a tubular condenser, from this through a second scrubber and then through two purifying boxes, $14 \times 14 \times 3$ feet with a twenty-four inch seal. From the purifiers the gas passes through the station meter and thence to the holder. The purifying material used is technically known as Laming's Mass, and is prepared by treating wood shavings with copperas and lime, four barrels of copperas and about the same amount of lime being used to 300 bushels of shavings.

TEMPERATURE.

The destructive distillation of the oil in the process of gas-making is an endothermic operation, large quantities of heat being taken up from the hot brickwork, and the operation can only be carried on for from seven to ten minutes at a time, when the heating must be recommenced and continued for approximately the same length of time.

The temperatures in the generator were measured by noting the melting-points of salts. The salt was wrapped in platinum foil; this was placed in a sheet iron tube attached to an iron rod and the insertion was made through a hole in the side of the generator.

Measurements of the lowest temperature were made by introducing the salts immediately after the gas-making ceased and withdrawing them at the end of two minutes. Sodium chloride was unaltered in all trials at the first temperature, potassium chloride fused in about three minutes, while potassium bromide melted in less than two minutes. The lower temperature is, therefore, between the melting-points of potassium bromide and potassium chloride.

At the highest temperature sodium carbonate fused but calcium fluoride was unaltered. Experiments with sodium sulphate were rejected because the salt was apparently reduced by the gases to which it was subjected.

In assigning a temperature in degrees some difficulty is experienced, as authorities differ as regards the melting-points of these salts. The following values are given by Carnelly,[1] and quoted in the work of Mills and Rowan on fuels, page 341, and by Victor Meyer, and Riddle.[2] The values of the latter, however, are stated as being preliminary only and the melting-point of sodium carbonate especially, is stated, in a later paper, to be too high.

	Carnelly.	Meyer and Riddle.
Potassium bromide		715° C.
Potassium chloride	734° C.	766° C.
Sodium chloride	772° C.	851° C.
Sodium carbonate	814° C.	1098° C.
Calcium fluoride	902° C.	

The lower temperature may be stated with some degree of certainty as being about 750° C., while the higher temperature is probably 900° to 1,000° C.

[1] *J. Chem. Soc.*, [London] *1878* and *1880*. [2] *Ber. d. chem. Ges.*, 26, 2443.

COMPOSITION OF THE GAS.

The following determinations of the technical composition of the gas were made with Orsat's apparatus, the determinations of methane and hydrogen being made by explosion with an excess of air and the addition of oxyhydrogen gas, the large amount of methane rendering an explosion with air alone almost impossible. The illuminants were determined by absorption in fuming sulphuric acid. The first two determinations were duplicated with Hempel's apparatus with almost identical results. The "total carbon" in the gas was determined by exploding a known volume of the gas with an excess of air and determining the volume of carbon dioxide formed. The ethylene and propylene are calculated on the assumption that the illuminants consist exclusively of these two gases. It is well known, of course, and will be further shown below, that this is not the case, but for the purpose of calculating the heat of combustion of the gas the error introduced is slight and is certainly less than on the assumption, usually made, that the illuminants consist entirely of ethylene.

The heat of combustion is calculated on the basis of one cubic foot of the gas at 0° C., burned to carbon dioxide and vapor of water. The following values are used, deduced from the values given in Winkler's "Technische Gasanalyse."

One cubic foot of	ethylene	gives	1573.3	English	heat	units.
" " "	propylene	"	2324.8	"	"	"
" " "	carbon monoxide	"	342.4	"	"	"
" " "	methane	"	964.3	"	"	"
" " "	hydrogen	"	289.8	"	"	"

	Feb. 20. Undiluted gas. Per cent.	Feb. 20. Diluted gas. Per cent.	May 22. Diluted gas. Per cent.	June 5. Diluted gas. Per cent.
Carbon dioxide	2.3	2.1	0.7	0.8
Illuminants	28.1	19.9	19.3	15.9
Oxygen	0.2	5.9	7.0	7.7
Carbon monoxide	0.6	1.8	0.0	0.0
Methane	44.8	32.3	33.2	36.0
Hydrogen	20.5	14.2	6.9	6.1
Nitrogen	3.5	23.9	32.9	33.5
	100.0	100.0	100.0	100.0
Total carbon—carbon dioxide	115.7	85.6	85.5	77.0
Illuminants { Ethylene	16.2	10.3	6.3	7.5
Illuminants { Propylene	11.9	9.6	13.0	8.4
English heat units per cubic foot	1025.0	744.0	741.0	678.0

The small amount of carbon dioxide and carbon monoxide present in the gas is worthy of especial remark. Steam is used to inject the oil into the generator, but the analyses show that the steam must pass out at the end almost entirely unchanged. It follows from this that in an atmosphere of reducing gases and at a temperature of 700° to 900° C. it is impossible to burn carbon to carbon monoxide or dioxide by means of steam. This is still more apparent in those forms of the process in which air is introduced into the generator. One of us has made many analyses of gases produced in that way and in every case the oxygen of the carbon dioxide and carbon monoxide combined was less than that of the air introduced. These facts have a very important practical bearing as regards the use of steam with petroleum in the manufacture of gas.

The gas directly from the producer contained 1.83 grains of sulphur per cubic foot. The purified gas contained 0.025 grain per cubic foot.

EFFICIENCY.

The amount of oil required for 1,000 cubic feet of gas varies somewhat with the condition of the generators. The following determinations were made:

I. Feb. 20. One run of the large generator when it was about to be shut down for repairs.

Oil per 1,000 cubic feet of diluted gas, for heating	...	2.3 gallons.
" " " " " " generating		10.7 "
Total		13.0 "

II. June 5. Average of five runs of the large generator just fitted with new brickwork.

Oil per 1,000 cubic feet of diluted gas, for heating	...	1.4 gallons.
" " " " " " generating		9.7 "
Total	...	11.1 "

On comparing the analyses, it will be seen that the gas of June 5 was diluted somewhat more than that of Feb. 22, so that the real difference in efficiency is only about six per cent. As the oil used was different and that of June 5 was, apparently, of better quality, no reliance can be placed on the difference.

So much time was taken for other parts of the work that these

determinations were not repeated so many times as they should have been. Apparently, however, about ten gallons of oil are used in the large generator for generating 1,000 cubic feet of diluted gas and 1.5 to 2.0 gallons of oil are used for heating. When we consider the amount of the dilution, these results are somewhat lower than those reported by Armstrong and Miller. Unfortunately they give no analyses of the gas.

The oil used on Feb. 20 contained some water and an analysis gave

	Per cent.
Carbon	81.0
Hydrogen	12.7

The specific gravity was 0.843.

The oil used on June 5 was nearly free from water and had a specific gravity of 0.865.

We will take the run of June 5 as a basis for calculating, approximately, the efficiency of its plant. If we assume the oil to contain eighty-six per cent. carbon and fourteen per cent. hydrogen one gallon of the oil would give, when burned to vapor of water, about 140,000 English heat units, and the amount of oil required for the manufacture of one cubic foot of gas would give about 1,550 English heat units. Since the gas itself gives 678 units per cubic foot (see analysis), about forty-four per cent. of the heating power of the oil is found in the gas.

Without going into the details of calculation, it may be of interest to state that about thirty-five per cent. of the heating effect of the oil used in heating the generator, is lost by reason of the high temperature of the smoke gases, and an approximately equal amount of heat is carried away by the gas during the generation of the latter. It is probable that at least ten per cent. of the heating effect of the total oil used is lost in this way, though the calculations do not show quite that amount. The remainder of the loss appears to be due mainly to the formation of tar.

PHOTOMETRIC TESTS.[1]

On May 21 a test of the candle-power of the diluted gas, as furnished to consumers, was made, using a Lumner-Brodhun

[1] These tests were made with instruments from the Physical Laboratory, and under the direction of Prof. C. L. Mees.

photometer with a three meter bar. The instrument was made by Hartman and Braun. The Methven slit was used as the direct standard, its value being first determined in terms of a standard amyl acetate lamp which was taken as of one candle-power. A wet meter, which, during one minute, indicated the number of cubic feet burned per hour, was used. Readings were taken on the meter and photometer each minute for five, and sometimes ten, consecutive minutes. Averages of these readings were made and the gas consumption was corrected for temperature.

The first night, tests were made using an argand, a five foot bat-wing, and a small and large Welsbach burner.

The second night, tests were made with a view to determining the relative efficiencies of different sizes of bat-wing burners, and of each size burning under different conditions. The conditions chosen were those of a smooth flame with a consumption rather under the indicated amount, and of a large, forked flame burning as high as possible without blowing. The appended table shows the results obtained,

MAY 22. METHVEN = 2.57 CANDLES.

Burner	Candle power found during the test.	Rate of gas burned per hour during the test.	Candle power corrected for five feet per hour.
Argand	29.3	5.17 cu. ft.	28.4
Five-foot bat wing	33.9	5.27 "	32.2
Small Welsbach	31.4	3.25 "	48.3
Large Welsbach	57.13	6.06 "	47.1

MAY 23. METHVEN = 2.36 CANDLES.

Nature of flame.	Burner.	As above.	As above.	As above.
Smooth	2 ft. bat wing.	14.20	3.21 cu. ft.	22.12
Forked	" "	23.32	5.54 "	21.05
Smooth	3 "	18.53	3.49 "	26.54
Forked	" "	30.02	6.32 "	23.75
Smooth	4 "	19.66	3.43 "	28.66
Forked	" "	37.45	6.74 "	27.78
Smooth	5 "	28.00	4.47 "	31.32
Forked	" "	39.88	6.43 "	31.01
Smooth	6 "	25.01	3.96 "	31.58
Forked	" "	45.01	7.06 "	31.87
Smooth	7 "	29.32	4.43 "	33.10
Forked	" "	53.18	8.27 "	32.15

It will be seen that the larger burners are most efficient and that, with one exception, the smooth flame gives better results. This is especially true of the smaller burners. A sample of the gas taken on May 22 gives for the calculated heating effect 741 English heat units. The statement of the analysis is given elsewhere.

COMPOSITION OF THE ILLUMINANTS.

In order to determine the presence and the amount of benzene and similar hydrocarbons in the gas, these were determined by a modification of the method of Hempel and Dennis, (see next paper), and also by absorption in absolute alcohol and subsequent dilution with salt water. Both methods gave essentially the same result and showed that about 1.2 per cent. by volume of the gas consists of the vapor of these hydrocarbons. From the oil obtained by the second method pure metadinitrobenzene was easily obtained by nitration and crystallization.

To determine the composition of the other gases forming the illuminants, gas directly from the generator was aspirated through an absorption train consisting of two one-liter bottles packed in ice to condense the tar, then two one-half liter bottles half filled with an ammoniacal solution of cuprous chloride to absorb acetylene, next a bottle of the same size half filled with dilute sulphuric acid to absorb ammonia fumes from the cuprous chloride solution, next three Drechsel wash-bottles standing in ice-water, the first two containing one hundred grams each of bromine with about half an inch of water above, and the third containing distilled water for the collection of bromine carried over from the other two, and finally a wash-bottle half full of a solution of sodium hydroxide to absorb bromine fumes. Approximately 125 liters of gas were passed through the train to effect the saturation of the bromine.

The bromine compounds were washed twice with caustic soda, then with distilled water, were separated, dried with calcium chloride, and fractioned. More than one-half came over between 127° and 150°. The residue remaining in the distilling bulb solidified on cooling. It was crystallized from alcohol and from ligroin when it melted at 113°–113.5°. An analysis gave the following results:

0.0750 gram gave 0.1500 gram AgBr.

	Cal. for $C_4H_8Br_4$.	Found.
Br.....	85.56	85.11

Armstrong and Miller[1] obtained a bromide melting at 116°, which they considered to be divinyl tetrabromide (1, 2, 3, 4 tetrabrombutane). The substance described above was probably the same, but less pure, as we have worked with much smaller quantities.

The portion of the bromides boiling from 127° to 150° was redistilled and gave three fractions, the largest 129°–133°, that from 133°–139° next and that from 139°–143° least. After fractioning again, a determination of the molecular weight by the air-displacement method of Victor Meyer, was made with the portion boiling at 130° to 133°. The results agreed fairly with the molecular weight of ethylene bromide. Determinations of the molecular weight of the fraction 140°–143° were unsuccessful owing to decomposition of the bromide. There can be little doubt, however, that the bromides consisted chiefly of ethylene and propylene bromides, the former being present in much larger amount than the latter.

A considerable precipitate was obtained in the ammoniacal solution of cuprous chloride, indicating the presence of appreciable amounts of acetylene and its homologues. In this respect our results differ from those of Armstrong and Miller.

TAR.

The amount and character of the tar varies considerably with the conditions of running. Two samples of the tar were examined, one which was thick and viscous, another which was comparatively thin. No essential difference in qualitative composition was established. The lower boiling substances contained in the tar were separated by distillation with superheated steam, the higher boiling products by direct distillation. In the direct distillation much trouble was experienced from frothing and it was found necessary to heat the tar at first in small quantities in an open dish until the frothing ceased. The residue was then distilled as usual.

Without going into the details of the work the results of the study may be stated briefly as follows:

[1] *J. Chem. Soc.*, (London) 49, 81, (1886).

Benzene and its lower boiling homologues appear to be present in the tar in only small amount. No positive evidence of their presence was obtained, although it has been shown that benzene is present in the gas.

Naphthalene is present in considerable amount and was identified by melting-point and boiling-point.

Anthracene is also present and was identified by melting-point and by conversion into anthraquinone. An approximate quantitative determination of the amount of anthracene was also made, showing the presence of about 0.35 per cent.

From the portion coming over at about 425° there was obtained, by crystallization, a solid melting at 250° and probably crysene.

From the portion boiling still higher a green crystalline solid melting at about 240° was obtained but not in sufficient amount for its identification.

Attempts to isolate phenol were unsuccessful, though it is probably present in small amount.

The results of the investigation confirm the conclusion of Armstrong and Miller that benzene and allied hydrocarbons may be formed, at high temperatures, from hydrocarbons which bear no simple relation to them.

In conclusion we wish to express to Mr. J. J. Kirkham, Superintendent of the Terre Haute Citizen's Fuel and Gas Company, our thanks for many favors shown us in the course of the work.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. V.]

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.[1]

BY W. A. NOYES AND W. N. BLINKS.

SOME time since Hempel and Dennis[2] described a method of determining benzene vapors in illuminating gas which depends on their absorption in a very small quantity of absolute alcohol. The amount of mercury required and the difficulty of applying the method as described by these authors led us to

[1] Read at the Brooklyn meeting, August 15, 1894.

[2] *Ber. d. chem. Ges.*, 24, 1162. Also the translation of Hempel's Gas Analysis by L. M. Dennis, p. 221.

attempt the determination with the use of a Bunte burette. The results were so satisfactory that it seems worth while to describe our method of procedure.

One hundred cc. of gas are taken in the burette and measured, either as usual, with a column of water of definite height above, or, perhaps better, with a side tube or bottle attached below so that the gas is brought to atmospheric pressure. The water is then completely removed from the cup of the burette above and the water in the burette is drawn down to the lower stop-cock as usual for the introduction of reagents. Instead of introducing the alcohol from below, however, two or three cc. of absolute alcohol are poured into the cup above and allowed to enter the burette, one cc. at a time. After each admission of the alcohol enough time is given for it to thoroughly run down before more is admitted and care is taken that the walls of the burette are uniformly moistened with the reagent. After withdrawing the alcohol below in the usual manner, two or three cc. of water are admitted above and withdrawn below and then more water is admitted above till the gas is brought to the original pressure, and the volume read.

To test the accuracy of the method, several determinations of the amount of benzene in the gas described in the last paper, were made. This gave 1.2, 1.3, 1.2, 0.5, and 1.2 per cent. The fourth determination was evidently in error for some unknown reason.

Twelve cubic feet of the same gas were passed through a meter, then through two large calcium chloride drying tubes, and then through three Drechsel wash-bottles containing absolute alcohol and a fourth empty bottle to condense vapor carried over, all being surrounded by ice. On dilution with salt-water, 16.8 cc. of liquid hydrocarbons were obtained. Considering these hydrocarbons to consist of benzene they would occupy in the form of vapor at 20° a volume of 4.46 liters. Twelve cubic feet are equal to 340 liters, of which 4.46 liters is 1.31 per cent. When we consider that a portion of the hydrocarbons obtained must have consisted of toluene, naphthalene and other hydrocarbons, whose vapors would occupy a smaller volume than benzene for a given weight, the agreement is satisfactory.

A DEVICE FOR THE ADJUSTMENT OF A BALANCE.[1]

By Frank T. Green.

Received July 27, 1894.

IT is a matter of surprise to intending purchasers that some sensitive balances lack a method of adjustment. I do not allude to the analytical balance only. The assay, prescription, or pulp balance, often has this important improvement wanting. It is well known that the method of adjusting by screws on one or both ends of the beam is satisfactory. Also, that by means of a flag on the top and center of the beam—frequently used by Oertling—a wonderfully close adjustment can be reached.

It is not the intention to criticise these methods, but rather to show how an instrument lacking these improvements can be made adjustable by a person not a mechanic.

By means of a small strip of metal, fashioned after Fig. 1, and

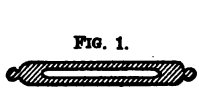


Fig. 1.



Fig. 3.

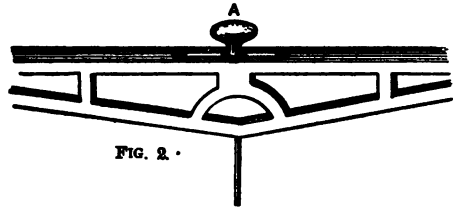


Fig. 2.

preferably made of brass, any balance having a center screw on top of beam A can be made adjustable.

Fig. 1 represents such a device to be fastened to the top of beam in the center in such a manner as to slide either to the right or left as required. When the point of adjustment is reached it can be fixed by tightening the central screw, Fig. 2.

The strip, Fig. 1, or the arrow, Fig. 3, can be made in a few minutes of tinned iron, brass, or sheet proof-silver. The latter metal always being at hand in an assay office. The arrow method being adjusted by turning either to the right or left.

[1] Read at the Midwinter Fair Congress of Chemists, San Francisco, June 8, 1894.

NOTE ON A FORM OF SILVER OBTAINED IN THE REDUCTION OF THE SULPHIDE BY HYDROGEN.[1]

By Francis C. Phillips.

Received July 2, 1894.

IT is a well-known fact that many of the metals are reduced from their oxides, sulphides, and other compounds by hydrogen at high temperatures.

In the majority of such cases the form in which the metal is set free depends upon its fusibility. When both the metal and its compound are fusible only at temperatures far above that at which reduction by hydrogen occurs, the reduced metal usually retains the form originally possessed by its compound, becoming, however, somewhat more porous. Iron reduced by hydrogen from the oxide, sulphide, or chloride, appears as a porous mass or fine powder. The same is true of platinum and of copper.

In the case of other metals, the character of the original compound may exercise a determining influence on the form of the metal after its reduction.

If silver chloride be heated in hydrogen to about 300° C., reduction occurs with formation of hydrogen chloride. The reduced silver appears as a compact, rounded mass, somewhat rough, and having a moderate degree of luster. On heating precipitated silver sulphide in hydrogen, a decomposition occurs with formation of hydrogen sulphide at about the melting-point of silver chloride (450° C.).

The reaction is slow at this temperature, but is more rapid at a somewhat higher heat. The dull, black powder soon begins to assume a slightly lustrous appearance, and at the same time changes gradually into a mass of tangled wires or threads, which lose the black color of the sulphide and exhibit the luster of highly burnished silver. These vary in thickness from that of the finest hairs to that of coarse sewing-thread. They are so linked and knotted together as to be almost inextricable. Under

[1] First printed in Proceedings of Chemical Section, Eng. Soc., W. Pa., April, 1894; communicated by the author.

a microscope it can be readily seen that some of these wires are made up of many smaller ones, which are often imperfectly twisted together, giving the appearance of a rope whose strands had become partly untwisted. Closely-wound coils are often visible. Many of the wires seem to have the smaller ones of which they are composed welded into a single wire, the sides of which then have a fluted or grooved appearance. Owing to the open spaces left in such a mass, a considerable expansion occurs during the reduction. In several trials it was found that the volume of the mass of reduced silver was about three times that of the original sulphide. Experiments made with argentite, the native silver sulphide, using a piece about three cm. thick, led to similar results. The facets of the crystalline mass did not change their shape, nor was their luster much diminished, but a great number of fine wires of lustrous silver seemed to grow out from the mineral in all directions.

Silver sulphide heated in natural gas gave results like those obtained in hydrogen.

Stephanite, Ag_5SbS_4, although fusible in hydrogen with evolution of a little hydrogen sulphide, yielded no silver at a temperature of dull redness.

Copper sulphide, artificially prepared, was slowly reduced by hydrogen at about the melting-point of barium nitrate (600°) with gradual formation of lustrous threads of copper very similar to those obtained in the case of silver.

The observation that silver and copper may be obtained in the form of wires by reduction of the sulphides is not new.

Opificius (*Chemiker Zeitung*, *1888*, 649) announced that such a change occurs.

Bischof (*Annalen der Phys. und Chem.*, *1843*, 289) describes experiments in which silver sulphide heated in steam to the temperature of boiling sulphur was reduced, yielding wire silver, the sulphur of the sulphide at the same time being oxidized to sulphuric acid. Bischof compares this change of crystalline argentite into wire-like forms of metal on reduction to the alteration of augite into asbestos.

Hampe (*Chemiker Zeitung*, *1893*, 1692) has shown that copper in moss-like forms is produced on heating copper sulphide

with filings of the metal to a temperature above the melting-point of copper. The author supposes that copper is dissolved by the fused sulphide and set free again on cooling, being forced out from the fluid interior through the pores of the nearly solid crust in wires or threads. Similar experiments by this author in heating silver with silver sulphide yielded the metal in form of imperfect crystals instead of wires. It is not easy to account for the fact that silver can assume the form of wires or threads so readily on reduction of the sulphide. The fusing-point of silver is 500° higher than the temperature of reduction, and it does not seem possible that the peculiar form of the silver can have been caused by fusion of the metal. Nevertheless, its appearance suggests that it has passed through a liquid or plastic condition. It might seem possible that by the heat of reaction between the silver sulphide and hydrogen silver, at the moment of its reduction, the silver had been heated locally to fusion. The heat of formation of silver sulphide (three calories) is, however, nearly as great as that of hydrogen sulphide 7.2 calories). Hence the heat of reaction could not suffice to fuse the silver. Nor does it seem probable that the quality of ductility of solid silver could be here brought into play, for there is apparently no force which could be supposed to cause a drawing out of the metal. Hampe's explanation, that by being forced out through pores in a solidified and contracting crust, covering a fused interior, copper may have been caused to assume the wire form, cannot apply to silver, for the process here is undoubtedly a gradual one, the sulphide passing without fusion, as reduction occurs, into the form of pure silver wires. The results obtained in laboratory experiments suggest an explanation of one mode of occurrence of native metals in veins.

The wire silver found at Zacatecas, in Mexico, may have originated from reactions of such a character.

Hausmann (*Eng. and Min. Jour.*, May 2, *1890*) describes the occurrence near Breckinridge, Summit County, Colo., of native gold possessing the remarkable wire-like forms, with fluted or grooved surfaces, so characteristic of silver and copper produced in the laboratory by the reduction of the sulphides by hydrogen.

The change into the fibrous condition at the temperature of

the puddling furnace, as cast-iron becomes converted by oxidation into puddled iron, may, perhaps, be considered similar to that which occurs in the reduction of silver sulphide by hydrogen.

The complete removal of impurities from the iron requires a temperature approaching fusion, and the fibers resulting as the metal becomes nearly pure are united into a mass.

THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

(*Continued from page 643.*)

Another portion of the bean-meal was extracted with a considerable quantity of one per cent. sodium chloride solution; the extract was filtered as clear as possible, and dialyzed in a large vessel containing alcohol. The globulin readily separated after a short time, in well-formed tetrahedral crystals mixed with amorphous matter. This precipitate was filtered off, treated for forty-eight hours with one per cent. sodium chloride solution, filtered clear and again precipitated by dialysis in alcohol, at first quite dilute, but afterwards of gradually increased strength. The substance now separated in large well-formed tetrahedral crystals, the edges of which were slightly curved. This precipitate was filtered off, washed with water, alcohol, and ether, dried and analyzed with results as follows:

PHASEOLIN, PREPARATION 18. CRYSTALS.

	I.	II.	Average.	Ash-free.
Carbon.....	50.98		50.98	52.70
Hydrogen.....	6.56		6.56	6.78
Nitrogen.....	16.21	16.10	16.16	16.71
Sulphur.....	0.33	0.29	0.31	0.32
Oxygen				23.49
Ash.....	3.27		3.27	
				100.00

As dilute acids precipitate proteid substance when added to the sodium chloride extracts of the ground beans, it was thought desirable to make some preparations by this method. Accordingly an extract was prepared by treating the meal with one per cent. sodium chloride solution, and after clearing as completely

as possible by subsidence and decantation, two-tenths per cent. hydrochloric acid was added until a considerable precipitate resulted. After standing some hours the precipitate was filtered off, dissolved in very dilute brine, filtered clear and precipitated by dilution. Only a small part of the substance separated. This preparation, 19, was then washed with water, alcohol and ether, dried and found to contain ash-free, 16.71 per cent. of nitrogen.

The filtrate from 19, when greatly diluted, gave a further precipitate, which, when filtered off and washed with water, alcohol and ether had the following composition:

PHASEOLIN, PREPARATION 20.

		Ash-free.
Carbon	51.85	52.20
Hydrogen	6.91	6.95
Nitrogen	16.15	16.26
Sulphur	0.51	0.51
Oxygen		24.08
Ash	0.68	
		100.00

It is evident that the same globulin was obtained by this method as by those previously followed. Next to be noticed are two preparations of phaseolin, made by diluting the sodium chloride extracts in the manner already described, redissolving the precipitates first obtained in salt solution, and again precipitating by dilution. Preparation 21, contained ash-free 16.65 per cent. of nitrogen.

PHASEOLIN, PREPARATION 22.

	I.	II.	Average.	Ash-free.
Carbon	52.24		52.24	52.55
Hydrogen	6.86		6.86	6.90
Nitrogen	16.03	16.06	16.05	16.14
Sulphur	0.58		0.58	0.58
Oxygen				23.83
Ash	0.58		0.58	
				100.00

The filtrate from 22 was then treated with two-tenths per cent. hydrochloric acid, until a considerable precipitate resulted. This was filtered off, washed with water, alcohol and ether, and analyzed with the following results:

PHASEOLIN, PREPARATION 23.

		Ash-free.
Carbon	51.34	52.12
Hydrogen	6.59	6.70
Nitrogen	15.96	16.21
Sulphur	0.58	0.59
Oxygen		24.38
Ash	1.48	
		100.00

One more preparation of this globulin was made with special reference to its purity. For this purpose a considerable quantity of the globulin was precipitated from a one per cent sodium chloride extract of the beans, and after filtering off, was twice dissolved in dilute sodium chloride solution and precipitated by dilution after filtering clear. The final precipitate was thoroughly washed with water, alcohol and ether and analyzed. When dried over sulphuric acid, the preparation was readily soluble in dilute sodium chloride solution, and consisted entirely of the unaltered phaseolin. Its composition is shown by the analysis of preparation 24.

PHASEOLIN, PREPARATION 24.

	I.	II.	Average.	Ash-free.
Carbon	52.45	52.52	52.49	52.75
Hydrogen	6.99	6.80	6.90	6.95
Nitrogen	16.52	16.39	16.46	16.57
Sulphur	0.56	0.44	0.50	0.50
Oxygen				23.23
Ash	0.69		0.69	
				100.00

The properties of phaseolin as shown by careful examination of preparation 24, dried over sulphuric acid, are as follows:

In cold or warm distilled water it is entirely insoluble.

In sodium chloride solution, and in very dilute acids and alkalies, it is very readily soluble to a clear solution.

Dissolved in ten per cent. sodium chloride solution, it is not precipitated by acetic, hydrochloric, nitric, or sulphuric acids, added in either minute or considerable quantities, although when dilute hydrochloric acid is added to the one per cent. sodium chloride extract of the beans, the phaseolin is precipitated.

Dissolved in large proportion in ten per cent. sodium chloride solution, the proteid is precipitated by adding much pure water.

Solutions of phaseolin in brine are completely precipitated by saturation with ammonium sulphate, but only slightly by saturation with magnesium sulphate or sodium chloride.

Potassium ferrocyanide and acetic acid together, give a precipitate.

With copper sulphate and caustic potash, the usual violet coloration is obtained, and with nitric acid, the xanthoproteic reaction.

Dissolved in ten per cent. sodium chloride solution and heated very slowly in a double water-bath, no turbidity occurs until the temperature is raised to 95°. This turbidity slowly increases as the temperature approaches 100° and after some time, a flocculent precipitate begins to develop, which even after heating for an hour is but slight.

Like other plant-globulins, phaseolin separates from warm concentrated solutions on cooling, and from salt solutions on dialysis, in the form of spheroids.

The striking resemblance in composition of this proteid to the "myosins" found in the seeds of maize and oats, and also to animal myosin, is shown in the following table:

	Phaseolin.	Maize myosin.[1]	Oat myosin.[2]	Animal myosin.[3]
Carbon.....	52.58	52.68	52.34	52.82
Hydrogen.....	6.84	7.02	7.21	7.11
Nitrogen.....	16.48	16.82	16.88	16.77
Sulphur.....	0.56	1.30	0.88	1.27
Oxygen.....	23.54	22.18	22.69	21.93
	100.00	100.00	100.00	100:00

The four proteids, although having many properties in common, as well as a similar composition, are yet characterized by differences so considerable, as to leave no doubt of the individuality of each.

The maize myosin and animal myosin differ from the other two, by their greater content of sulphur, and also in coagulating, the former at 70° and the latter at 55° C.

Phaseolin presents many points of difference from the oat myosin. It is not precipitated from solutions in ten per cent.

[1] *Am. Chem. J.*, 13, 536.

[2] Report Connecticut Agricultural Experiment Station for *1890*, 137-160; also *Am. Chem. J.*, 13, 389; also Report Connecticut Agricultural Experiment Station for *1891*, 135.

[3] Studies from Laboratory of Physiological Chemistry, Yale University, 3, 133

sodium chloride by acids, and but slightly by saturation with sodium chloride, and is thrown down, both by dilution and by dialysis, with much greater difficulty than the oat myosin.

SUMMARY OF ANALYSIS OF PHASEOLIN FROM THE KIDNEY BEAN.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Carbon.....	52.23	52.60	52.60		52.54			52.72	52.35
Hydrogen...	6.95	6.69	6.72		6.83			7.24[1]	6.89
Nitrogen....	16.37	16.56	16.17	16.12	16.48	16.23	16.87	16.45	16.52
Sulphur	0.62	0.63	0.63		0.58			0.67	
Oxygen.....	23.83	23.52	23.88		23.57			22.92	24.24
	100.00	100.00	100.00		100.00			100.00	100.00

	10.	11.	12.	13.	14.	15.	16.	17.	18.[2]
Carbon.....	52.74	52.49		53.06	52.49	52.47	53.22		52.70
Hydrogen...	6.84	6.80		6.85	6.73	6.90	6.86		6.78
Nitrogen....	16.65	16.85	16.67	16.68	16.45	16.00[1]	16.48	16.29	16.71
Sulphur	0.64	23.86		23.41	24.13	24.63	0.48		0.32
Oxygen.....	23.13						22.96		23.49
	100.00	100.00		100.00	100.00	100.00	100.00		100.00

	19.	20.	21.	22.	23.	24.	Average.	Ritthausen.
Carbon.....		52.20		52.55	52.12	52.75	52.58	52.55
Hydrogen...		6.95		6.90	6.70	6.95	6.84	7.09
Nitrogen....	16.71	16.26	16.65	16.14	16.21	16.57	16.48	16.18
Sulphur		0.51		0.58	0.59	0.50	0.56	0.43
Oxygen.....		24.08		23.83	24.38	23.23	23.54	23.75
		100.00		100.00	100.00	100.00	100.00	100.00

PREPARATION OF PHASELIN.

Proteid Remaining in Solution after Separation of the Globulin Just Described.

After precipitating phaseolin by the various methods employed in making the foregoing preparations, the extracts contained proteid matter which could be separated by dialysis in distilled water, by adding acids and by prolonged heating.

These methods of precipitation gave products of nearly uniform composition, except in those cases where the phaseolin had been incompletely separated. Preparations of phaselin were accordingly made as follows:

When a portion of the dialyzed solution from which preparation 1 had been separated, was heated slowly it became turbid

[1] Omitted in making average.

[2] Tetrahedral crystals.

at 40°, flocks appearing at 68° in considerable quantity. When filtered, after heating at 72°, a second turbidity was obtained at 83°, and flocks formed at 87° in greater quantity than at 68°. The remaining solution was dialyzed in alcohol until its volume was reduced by one-half. An equal bulk of strong alcohol was then added to the contents of the dialyzer, and the mixture allowed to stand until the precipitate settled. After three days the solution was decanted and the precipitate washed with absolute alcohol and ether and dried over sulphuric acid. The substance, thus dried, weighed eleven grams. It was finely ground, thoroughly extracted with distilled water, and this extract filtered from the large insoluble residue. The clear solution was then found to become turbid when heated to 63° and to yield a flocculent coagulum at 76°. The entire solution was therefore heated for several hours in a water-bath at 80°, and the coagulum filtered off, washed thoroughly with water, alcohol and ether and dried over sulphuric acid. The 0.9 gram of substance thus obtained, was dried at 110° and analyzed with the following result. Preparation 25.

PHASELIN, PREPARATION 25.

		Ash-free.
Carbon	51.67	51.96
Hydrogen	6.67	6.71
Nitrogen	15.55	15.65
Sulphur } Oxygen }		25.70
Ash	0.57	
		100.00

When the filtrate from 25 was again heated to 80°, a further coagulum resulted. The solution was accordingly kept at this temperature as long as any coagulum was produced, filtered, and the coagulum washed with hot water, alcohol, and ether, and dried for analysis at 110°. This preparation, 26, contained, ash-free, 14.57 per cent. of nitrogen and weighed 0.71 gram.

Two other preparations were made from the filtrate from preparation 3, in nearly the same way as the two last described, the only difference being that the solution was precipitated with alcohol without first concentrating by dialysis in alcohol.

The first coagulum, preparation 27, obtained by heating at

80°, weighed only 0.17 gram, and when dry contained without correction for ash, 14.90 per cent. of nitrogen. The second weighed one gram and had the following composition:

PHASELIN, PREPARATION 28.

		Ash-free.
Carbon	51.19	51.57
Hydrogen	6.87	6.92
Nitrogen	14.36	14.48
Sulphur } Oxygen }		27.03
Ash	0.75	
		100.00

After largely diluting, the filtrate from preparation 16 failed to give any further precipitate on passing carbon dioxide through it for some time. The greater part of this solution was then thrown away, but by chance a little acetic acid was added to the remainder and found to produce a precipitate. This precipitate was filtered off, washed with water, alcohol, and ether, and when dried, weighed 0.27 gram and contained without correction for ash, 14.81 per cent. of nitrogen. Preparation 29.

Another preparation was then made by extracting bean meal with one per cent. brine, diluting the extract with a large quantity of water, and filtering off the precipitate. The filtrate was then treated with two-tenths per cent. hydrochloric acid until a considerable precipitate resulted, which was filtered off and the solution again treated with two-tenths per cent. hydrochloric acid. This final precipitate was filtered off, washed with alcohol and ether and gave one gram of preparation 30, having the following composition:

PHASELIN, PREPARATION 30.

		Ash-free.
Carbon	50.18	51.38
Hydrogen	6.53	6.71
Nitrogen	14.44	14.84
Sulphur } Oxygen }		26.87
Ash	2.74	
		100.00

Again, the filtrate from preparation 10, was treated with an equal volume of strong alcohol and allowed to stand over night.

The next morning, the precipitate which had separated was filtered off and treated with water. This dissolved some of the substance. This solution, filtered clear, when heated, gave a flocculent coagulum at 80°. With acetic, hydrochloric, or nitric acid, it gave a precipitate when the reagents were added in sufficient quantity. These precipitates were soluble in sodium chloride solution, and those produced by hydrochloric and nitric acids, were soluble in an excess of the acid, but that given by acetic acid, was not noticeably soluble in an excess. The precipitate obtained with nitric acid, did not dissolve upon warming, as is the case with such precipitates yielded by proteoses. The reaction of the extract was slightly acid, but it was not possible to precipitate anything therefrom, by the most careful neutralization. The whole solution was then treated with two-tenths per cent. hydrochloric acid; the precipitate thus formed had the following composition:

PHASELIN, PREPARATION 31.

		Ash-free.
Carbon	49.91	51.98
Hydrogen	6.55	6.82
Nitrogen	13.95	14.53
Sulphur } Oxygen }		26.68
Ash	4.00	
		100.00

The precipitate from which 31 was derived, after this extraction with water, was but slightly soluble in sodium chloride solution, and was therefore treated with two-tenths per cent. potash water. The resulting solution was filtered clear, and hydrochloric acid cautiously added, until a precipitate formed which was collected on a filter and treated in the usual manner. When dry, this preparation, 32, weighed 3.3 grams.

The filtrate from 32 was further treated with two-tenths per cent. hydrochloric acid, and a second precipitate obtained which weighed 0.6 gram; preparation 33.

PHASELIN, PREPARATION 32.

	I.	II.	Average.	Ash-free.
Carbon	51.74	51.74	51.74	52.65
Hydrogen	7.04	7.00	7.02	7.14
Nitrogen	14.89		14.89	15.15

	I.	II.	Average.	Ash-free.
Sulphur }				25.06
Oxygen }				
Ash	1.78		1.78	
				100.00

PHASELIN, PREPARATION 33.

		Ash-free.
Nitrogen	14.24	14.85
Ash	4.12	

Another preparation was made by extracting 100 grams of bean meal, with 100 cc. of one per cent. sodium chloride solution, and washing the insoluble residue with 100 cc. of the same solution, applied in successive portions. The entire extract was then filtered nearly clear, and dialyzed in alcohol. The alcohol of the outer vessel was frequently renewed, and the process was continued until practically all the proteid matter had separated. The precipitate was then filtered off and extracted with one per cent. sodium chloride solution. Much of the substance remained undissolved. The solution was filtered clear and dialyzed again in alcohol of 0.85 sp. gr. which was renewed once during the process. The precipitate resulting was filtered off and washed with dilute alcohol, absolute alcohol and ether and dried at 110°. Its composition was as follows:

PHASELIN, PREPARATION 34.

		Ash-free.
Carbon	46.49	51.38
Hydrogen	6.25	6.91
Nitrogen	13.27	14.67
Sulphur }		27.04
Oxygen }		
Ash	9.53	
		100.00

In order to obtain a purer preparation of the proteid by this method, 200 grams of bean meal, first extracted with petroleum-benzine, were treated with one liter of one per cent. sodium chloride solution and after squeezing out, the residue was mixed with another liter of the same solution and again squeezed. After standing over night, the turbid extract was decanted and dialyzed in alcohol for three days, the alcohol being once renewed. This treatment precipitated nearly all the proteids, which were

collected on a filter, and after the solution had run off, the precipitate was suspended in one-quarter per cent. sodium chloride solution, filtered off and washed with the same solution. The clear filtrate and washings were then dialyzed into alcohol until a considerable precipitate had formed which was filtered off and washed successively with fifty per cent. alcohol, stronger alcohol, absolute alcohol, and ether, and dried over sulphuric acid. It was then almost wholly soluble in water, but after drying at 110° it became insoluble, and was washed with water, alcohol, and ether, and again dried, 35.

PHASELIN, PREPARATION 35.

	I.	II.	Average.	Ash-free.
Carbon	49.01		49.01	51.37
Hydrogen	6.77		6.77	7.10
Nitrogen	14.26	13.82	14.04	14.71
Sulphur } Oxygen }				26.82
Ash	4.58		4.58	
				100.00

[TO BE CONTINUED.]

THE DETERMINATION OF ALBUMEN IN COW'S MILK.

BY L. L. VAN SLYKE.

Received August 22, 1894.

IN Vol. 15, No. 11 of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, the writer presented a paper on the determination of casein in cow's milk. It is now desired to present another paper supplementary to that and relating to the determination of albumen in cow's milk.

Ordinarily, when we speak of milk albumen, we mean the portion of nitrogen compounds not coagulated by rennet, acid, etc. In other words, we apply the term albumen to the nitrogen compounds left after removing the casein proper. This use of the term albumen is inaccurate, because, after removing from normal milk its casein, there remain, at least, two nitrogen compounds or classes of nitrogen compounds. One of these is coagulated by heat, especially in the presence of dilute acids, while the other is not coagulated under these conditions. To the former only of these two, the term albumen is properly applicable.

DETAILS OF METHOD.

The filtrate obtained, after separating the casein by the method described in the article above referred to, is placed in a water-bath heated to the boiling temperature of water, the beaker containing the filtrate being covered with a watch-glass crystal. The solution is kept at this temperature until the albumen coagulates and settles to the bottom, leaving the supernatant liquid clear. Ten or fifteen minutes usually suffices to accomplish this. The precipitate is filtered, washed and then treated according to the Kjeldahl method for determining nitrogen. The amount of nitrogen multiplied by the factor 6.25 gives the amount of albumen.

It was thought that too long boiling of the albumen precipitate might cause some of it to redissolve; and, in order to ascertain what effect the length of time of heating influenced the results, the digestion was varied from five minutes to ten hours. The tabulated results are as follows:

	Length of time solution containing albumen was heated.									
	5 Minutes.	10 Minutes.	15 Minutes.	20 Minutes.	30 Minutes.	45 Minutes.	1 Hr.	2 Hrs.	4 Hrs.	10 Hrs.
No. of sample of milk.	Per cent. of nitrogen in albumen contained in milk.									
1 *a*		0.060		0.057	0.054	0.056	0.057	0.061	0.046	0.060
" *b*		0.062	0.058	0.048	0.051	0.063	0.062	0.059	0.055	0.054
" Average		0.061	0.058	0.053	0.053	0.059	0.059	0.060	0.051	0.057
2 *a*	0.014	0.054	0.054	0.052	0.052	0.051	0.052	0.047	0.045	
" *b*	0.044	0.053		0.054	0.051		0.051	0.051	0.049	
" Average	0.029	0.053	0.054	0.053	0.052	0.051	0.051	0.049	0.047	
3 *a*	0.054	0.053	0.049	0.052	0.051	0.053	0.057	0.057	0.056	0.058
" *b*	0.054	0.047	0.053	0.056		0.057	0.057	0.060	0.053	0.055
" Average	0.054	0.050	0.051	0.054	0.051	0.055	0.057	0.058	0.055	0.056
4 *a*	0.057	0.064	0.061	0.061	0.065	0.065	0.062	0.062	0.069	0.065
" *b*	0.062	0.055	0.065	0.063	0.064	0.062	0.065	0.066		0.065
" Average	0.059	0.060	0.063	0.062	0.064	0.063	0.063	0.064	0.069	0.065
Average of all results	0.047	0.056	0.056	0.055	0.055	0.057	0.057	0.058	0.056	0.059

An examination of the foregoing table shows:

(1) In one case, heating for five minutes gave low results; in two other cases, good results.

(2) In general, the results varied little with increased length of time of heating.

(3) There was a slight tendency to higher results with

increased length of heating, but such increase was more or less irregular and, at most, amounted to only 0.002 or 0.003 per cent. of nitrogen.

(4) It would, therefore, appear that entirely satisfactory results can be obtained by heating the solution containing albumen under the given conditions for ten or fifteen minutes, while an increased length of time of heating does not practically change the results.

It may be stated that the precipitate formed always filters readily and washes easily.

SEPARATION AND DETERMINATION OF THE NITROGEN COMPOUNDS OF COW'S MILK.

Below we give a brief summary of our method as we employ it in effecting the determination and separation of the three classes of nitrogen compounds present in the normal milk of cows.

1. Total Nitrogen Compounds.—Determine the amount of total nitrogen by the Kjeldahl method and multiply by the factor 6.25.

2. Casein.—Weigh out about ten grams of milk, dilute in a beaker with about ninety cc. of water at 40°–42° C., and add at once 1.5 cc. of a solution containing ten per cent. of acetic acid, by weight. Stir with a glass rod and let stand three to five minutes longer. Then decant on a filter, wash two or three times with cold water by decantation and then transfer precipitate completely to filter. Wash once or twice on filter. The washed precipitate and filter paper are then digested as in the regular Kjeldahl method for the determination of nitrogen, and the determination completed in the usual manner. To calculate the nitrogen into an equivalent amount of casein, multiply the amount of nitrogen by the factor 6.25.

3. Albumen.—The filtrate obtained above in separating casein is placed in a water-bath and heated to the boiling temperature of water for ten or fifteen minutes. The filtered and washed precipitate is then treated by the Kjeldahl method for determining nitrogen. The amount of nitrogen multiplied by 6.25 gives the amount of albumen.

4. Remaining Nitrogen Compounds.—The remaining compound or compounds of nitrogen are determined by difference,

subtracting from the amount of total nitrogen compounds the sum of the casein and albumen.

In conclusion, I wish to call attention to the crude nomenclature in common use in stating the results of milk analysis for nitrogen compounds. It is an almost universal custom to call the total nitrogen compounds of milk casein. It would be quite as correct to call the fat of milk palmitin or some similar name. This wrong use of the term casein leads to much confusion, and it is highly desirable that we should use a more discriminating nomenclature. It is also desirable that, in making analysis of milk, pains should be taken to separate and determine the different kinds of nitrogen compounds, since our knowledge of these compounds is far from complete.

I am much indebted to Mr. A. L. Knisely for assistance rendered by him in carrying out the analytical details of the work.

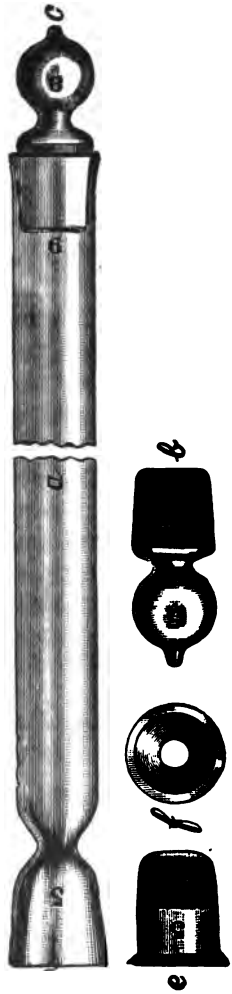
AN APPARATUS ("LYSIMETER") FOR DETERMINING SOLUBILITIES.

By Charles Rice.

Received July 11, 1894.

IN determining the solubility of a substance in some liquid at a given temperature, there is usually but little difficulty encountered when the solvent is not very volatile and the temperature at which the determination is to be made is not high. With a highly volatile solvent, and a high temperature, however, certain difficulties present themselves which are liable to lead to error. The main difficulty is encountered in the endeavor to separate from the original solution, which usually contains an excess of the substance in suspension, a *filtered* portion at the same temperature as that of the solution. The higher this temperature is, the more difficult becomes the removal of a portion without the introduction of errors by the ordinary methods of filtration. It appears, therefore, that it is only necessary to modify the method of filtration in such a way as to maintain the temperature of the original solution unchanged in order to eliminate these errors. This may be easily accomplished by upward filtration into a tube placed in the original solution, and so constructed that it will enable the operator to control the act of filtration, as well as accurately to determine the amount of solvent

and dissolved material. For this purpose the little apparatus here described has been found very serviceable.



The apparatus consists of a glass tube *a*, fifteen cm. long and one cm. in external diameter, provided at one end with a well-ground stopper *c*, while the other end is cup-shaped, there being a contracted neck between the cup and the main tube. Into this cup is made to fit, a carefully ground glass bell *e*, having a perforation in its bottom (as shown in *f*). There is also a stopper *b* which is carefully ground to fit into the cup, and which is inserted after the glass bell *e* has been removed. The several stoppers, etc., are all numbered to show where they belong.

To show how the apparatus is used it will be best to quote a practical example.

Let us assume that the solubility of morphine in boiling alcohol is to be determined. It will be necessary to provide for such an amount of liquid that at least one-half of the glass tube *a* may be immersed in the liquid. In the case of comparatively cheap solvents and substances to be dissolved, beaker glasses may be used; for more expensive materials, test-tubes of such a size that there will be no great waste of material are preferable.

The glass tube is made ready by inserting the stopper *c*, and introducing into the cup-shaped end the glass bell *e*, containing a pellet of purified cotton and prevented from dropping out by a thin platinum wire fastened around the contracted neck and crossed over the mouth of the bell. A sufficient amount of alcohol having been introduced into a beaker, or test-tube, heat is applied and morphine added until, after the boiling has been kept up some time, a portion of the alkaloid remains

undissolved. The prepared glass tube is now inserted in the liquid. As long as the stopper *c* closes the mouth of the tube no liquid will be able to filter upwards. When the tube has acquired the temperature of the boiling liquid the stopper *c* is removed, whereupon the liquid will begin to filter through the pellet of cotton and rise in the tube as far as the quantity of liquid will permit. In order to insure perfect uniformity of the liquid within and without the tube, it is best to allow the filtered portion to flow back through the pellet of cotton once or several times. The stopper *c* having then been inserted, the tube is withdrawn, turned upside down, the glass bell removed, and the stopper b inserted. The tube is now carefully cleaned with alcohol, and laid aside until cold. Its tare having previously been determined, the increase in weight represents the weight of the solution contained therein. On transferring or washing the contents into a tared beaker or capsule and evaporating, the weight of the dissolved morphine will be found.

The apparatus here described, which has been frequently in use during several years, and to which, for brevity's sake, the name *lysimeter* (from the Greek *lysis*, solution) has been given, was made for the writer in a very satisfactory manner by Mr. Emil Greiner, of New York City.

NEW YORK, July 7, 1894.

NEW BOOKS.

THE DECOMPOSITION OF THE FIXED ALKALIES AND ALKALINE EARTHS. By Humphry Davy, 1807–1808. Alembic Club Reprint, No. 6. 12 mo. 51 pp. Edinburgh: William F. Clay. 1894.

This number of the Alembic Club Reprints contains the Bakerian Lecture delivered by Davy before the Royal Society in 1807, and also part of a paper communicated by him to the same Society in the following year. The Bakerian Lecture is on the Decomposition of the Fixed Alkalies and on the General Nature of the Alkaline Bodies. The other paper is on the Decomposition of the Earths, with observations on the metals obtained from the alkaline earths.

In the first paper we have the first published record of the experiments by which Davy proved the compound nature of the alkalies and prepared the metals potassium and sodium. The

second paper contains a description of similar experiments upon the earths and alkaline earths, only that part which deals with the successful experiments being reprinted. W. R. O.

THE DISCOVERY OF OXYGEN. By Joseph Priestley, 1775, and Carl Wilhelm Scheele, 1777. Being Nos. 7 and 8 of Alembic Club Reprints. Edinburgh: William F. Clay. 1894.

Among the first things learned by students in chemistry, is that "oxygen was discovered almost simultaneously by Priestley in England, in 1774, and Scheele, in Sweden, in 1775." That the work of these men was independent of each other is also well known. Many have become acquainted with their work in a general way, but few have had the opportunity of following the original experiments as described by the experimenters. This opportunity is offered now by the publishers of the Alembic Club Reprints. Nos. 7 and 8 of this series are the Discovery of Oxygen. Part I (No. 7) by Joseph Priestley, and Part II (No. 8) by Carl Wilhelm Scheele, the latter a translation. They consist of sections taken from larger works of these authors, and, save for a short preface by the publisher, are without note or comment. Both Priestley and Scheele are minute in the description of the numerous experiments carried out in this work.

They began experimenting at different ends of the subject. Priestley was of the "try something" type of worker, and in his different experiments the peculiarities of "dephlogisticated air," as he afterwards called it, "obtruded themselves upon him." He first obtained the "air" then studied its properties. He tried to obtain this "air" from every available substance. The bulk of it was obtained from mercuric oxide and red lead and nitric acid. Scheele, on the other hand, found that air was not a simple substance, but contained a gas, which he called "fire air." The experiments which were performed when this truth was discovered are well described. They consisted in placing oxidizable substances in bottles which were well corked, and allowing the air in them to act for different periods of time, then opening the bottles under water and noting the diminution in the volume of air by the water entering the bottles. Then the work of producing "fire air" was undertaken, numerous experiments were carried out, the results of which are well known.

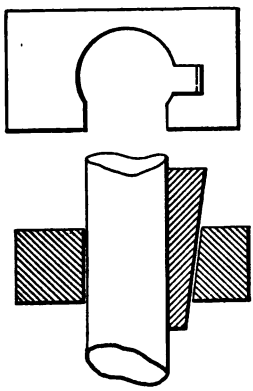
These two men had the theory of combustion in their grasp, and almost explain it in their writings, that they were unconscious of this fact is surprising.

The publishers of these Reprints are to be thanked for placing before the chemical world the work of these two men in such a handy and attractive form. A digest of a work is good, but the original furnishes the only true satisfaction. So these little books should be extremely valuable to the student, by enabling him to see the discovery of oxygen in its original shape.

OWEN L. SHINN.

NOTES.

Convenient Burette Clamp.—A convenient form of burette holder may be made from the appended sketch. A simple wedge being employed in place of the screw clamp to hold the tube in position. The surface of the wedge bearing on the tube should be slightly curved to ensure accurate contact. Cork is not necessary on bearing parts, as very slight pressure on upper end of wedge causes the tube to be held with great rigidity. Holder should be made of maple, wedge of hickory or other hard wood.—*Clarence Quinan.*



A New Atmospheric Element.—Lord Rayleigh and Professor Ramsay announce the discovery of a supposed new element contained in the atmosphere to the extent of about one per cent. Two methods of separation have been used. The first method consists in passing high tension electrical sparks through a mixture of equal bulks of air and oxygen confined over potash solution until no further diminution in volume ensues. The excess of oxygen is then absorbed by alkaline pyrogallate. The second method consists in removing the oxygen from air by red hot copper and the nitrogen by heated magnesium. The remaining gas has a sp. gr. of 18.9 and is more inert than nitrogen.

Wm. Crookes has examined the spectrum of the gas when the

induction spark is passed through a tube containing the new gas under an exhaustion of eight mm., and finds that "the spectrum is a very definite and characteristic one, and the lines differ in position from those of nitrogen. The appearance more resembles a metallic spectrum, and no flutings similar to those of nitrogen are to be seen." Professor Dewar suggests that the new element may be an allotropic form of nitrogen analogous to red phosphorus, and that the processes of preparation may be really methods of manufacture. E. H.

The Post-Mortem Detection and Estimation of Strychnine—Allerton S. Cushman. (*Transactions of the Academy of Science of St. Louis*, **6**, 537.)

The author recommends the following method for the detection and estimation of strychnine in toxical cases: The mass to be examined is comminuted and digested over night at a warm temperature with water acidulated with acetic acid, filtered through muslin and then through paper, the solution evaporated, an excess of eighty per cent. alcohol added, boiled, filtered, and extraction repeated. The liquid is then evaporated, the residue taken up with water and a little acetic acid, and the solution shaken repeatedly with acetic ether, as long as anything is extracted—twelve extractions may be necessary. A volume of acetic ether equal to that of the solution is now added, and sodium carbonate to alkaline reaction. After shaking, the acetic ether is separated and the extraction repeated. The strychnine is usually moderately pure as obtained by the evaporation of the acetic ether, but for quantitative estimation it is dissolved in dilute acetic acid, filtered, the solution extracted with ether-chloroform (1:1), ammonia added, and the extraction with ether-chloroform repeated twice. The residue obtained by evaporating the ether-chloroform is nearly pure and is weighed. Two experiments with known amounts of strychnine mixed with considerable amounts of meat, sugar, starch, and water, and allowed to stand in a warm place for two weeks, gave a recovery of about eighty-seven per cent. of the strychnine present. Directions for chemical, crystallographic, and physiological tests are given. Two toxical cases in which the method was applied are also given. W. A. NOYES.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

A METHOD FOR DETERMINING CALCIUM OXIDE IN QUICKLIME.

BY W. E. STONE AND F. C. SCHEUCH.

Received September 1, 1894.

THE value of quicklime is based upon the amount of calcium oxide which it contains. This value may be diminished by the presence of other substances originally present in the limestone, consisting usually of magnesia, alumina, silica, and iron; by incomplete ignition in the lime-kiln, on account of which some calcium carbonate fails to be converted into calcium oxide; and lastly, by a partial "slaking," by which a portion of the calcium oxide reverts to calcium carbonate.

An analysis of quicklime, therefore, should show not only the amount of calcium present in distinction from other elements, but should distinguish between the calcium as oxide and other forms of combination. The customary gravimetric method, based upon solution of the calcium compounds in acids, precipitation as calcium oxalate, ignition, etc., attains only the first of these requirements and affords no data for judging of the original condition of the calcium thus found. Consequently this method may furnish erroneous conclusions with regard to the commercial value of the material examined.

The method here proposed enables one to determine with a high degree of accuracy and rapidity the actual amount of calcium oxide in quicklime. It is based upon the well-known fact that

the alkaline earths form definite compounds with sucrose, called saccharates. Several such compounds are known with barium and strontium. With calcium oxide, sucrose forms at least three compounds, the mono-, di- and tricalcium saccharates, containing respectively one, two, and three molecules of calcium oxide to one of sucrose. The two first are formed when quicklime is dissolved in the cold in a sucrose solution. On heating this to boiling, a precipitate is thrown down consisting in the main of the tricalcium saccharate.

Numerous authorities may be quoted with regard to the solubility of calcium oxide in sucrose solutions of which the two following will suffice for citation.

Berthelot[1] gives the maximum solubility in solutions of sucrose of varying strength.

Grams sugar in 100 cc...	0.096	0.400	1.058	1.386	2.000	4.850
CaO dissolved.....	0.154	0.194	0.281	0.326	0.433	1.031

The following data are from Schatten.[2]

In ten grams of sugar solution of different percentages:

Per cent.....	1.	4.	8.	12.	16.
Grams CaO dissolved,	0.029	0.080	0.160	0.271	0.394

Numerous other references indicate the ready solubility of calcium oxide in sucrose solutions, and the apparent possibility of applying this fact to the separation of the actual calcium oxide from the other constituents of quicklime, led us to make the following studies:

1. The conditions under which calcium oxide is dissolved in sucrose solutions:

Lamy[3] has shown that solubility varies inversely with the temperature. Ten liters of ten per cent. sucrose solution, at the given temperatures, dissolved the stated amounts of calcium oxide.

Temperature C°.....	0°	15°	30°	50°	70°	100°
Grams CaO dissolved.....	250	215	120	53	23	15.5

For our experiments, pure calcium oxide was prepared by igniting pure calcium carbonate to a constant weight. It was

[1] *Ann. Chim. phys.*, [3], 46, 176.
[2] Von Lippmann, Die Zucker-Arten, 109.
[3] *La Sucrerie indigene et Coloniale*, 11, 19.

found by repeated experiment that one gram of this material was easily soluble in 150 cc. of a ten per cent. sucrose solution after agitating fifteen to twenty minutes at ordinary temperature. To accomplish perfect solution it was necessary that the material be finely pulverized. If heat were employed, the lime was converted into a pasty, insoluble mass which, however, dissolved on cooling.

2. The degree of solubility of calcium oxide in sucrose solution. Repeated experiments gave the following results:

One gram of pure CaO was only partly dissolved in 100 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 150 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 100 cc. of a ten per cent. sugar solution.

One gram of pure CaO was completely dissolved in 150 cc. of a ten per cent. sugar solution.

From these results it appears that not less than 150 cc. of a ten per cent. solution of sucrose could be safely employed to dissolve the calcium oxide in one gram of quicklime.

3. Behavior of other constituents of quicklime toward sucrose solutions:

Besides calcium oxide, quicklime usually contains more or less iron, alumina, magnesia, and silica. In addition to these, calcium carbonate may also be present. The behavior of these toward sucrose solutions was studied in detail with the following results:

Magnesia. Pure magnesium oxide, specially prepared, was treated with a ten per cent. solution of sucrose. One hundred and fifty cc. of the latter, after shaking with one gram of magnesium oxide for thirty minutes, were filtered and treated with ammonia and sodium phosphate, but only the faintest turbidity resulted. Again, one gram of magnesium oxide was shaken with 150 cc. of sucrose solution, filtered, and the filtrate titrated with standardized hydrochloric acid, and an equivalent of 0.001 gram of magnesia was found, or one-tenth of one per cent. These results show that magnesia is not appreciably soluble under the given conditions. Indeed, the existence of a com-

pound between magnesia and sucrose is doubted. On the other hand, magnesia is said to be freely soluble in a solution of calcium oxide in sucrose.[1] To test this point, mixtures of pure magnesium and calcium oxides were treated with sugar solutions as follows: One-half gram of each were mixed and shaken with 150 cc. of sugar solution. A considerable portion of the material was insoluble. We filtered and titrated the filtrate with standardized acid, the result being an exact equivalent of the calcium oxide employed. Again, one-half gram of each were mixed and treated with sugar solution as before. We filtered and precipitated the calcium from the filtrate by means of ammonium oxalate. The filtrate from this showed only slight turbidity when treated with ammonium and sodium phosphate. These results show that magnesium oxide is not soluble to an appreciable degree in sucrose solution containing calcium oxide, under the stated conditions.

Alumina was found quite insoluble, no appreciable amount being found in the filtered sucrose solution.

Calcium carbonate was also insoluble to any appreciable degree in the ten per cent. sucrose solution under the stated conditions.

Ferric oxide shaken with ten per cent. sugar solution was also insoluble. Schachtrup and Spunt[2] mention that ferric oxide inverts sucrose but not in an alkaline solution. We have verified this by heating a small quantity of ferric oxide with a sugar solution; the latter soon acquired the power of reducing Fehling's solution. But when the same experiment was repeated with the addition of some calcium oxide no inversion occurred. It is evident, therefore, that the iron contained in quicklime would not be affected by sucrose solution.

4. The determination of calcium oxide when dissolved in sucrose solution:

Calcium oxide when dissolved under the preceding conditions admits of determination, either gravimetrically by precipitation as calcium oxalate or volumetrically by titration with hydrochloric acid. Several comparisons of the two methods were made, using known amounts of pure calcium oxide and while

[1] Von Lippmann, *Die Zucker-Arten*, 148.

[2] *Pharm. Cent. Halle*, 34, 148.

each were accurate to the extent of yielding the theoretical numbers, the volumetric method was found preferable on account of its greater rapidity. For the latter method, standardized hydrochloric acid of about fifth-normal strength was employed, using tropaeolin or rosolic acid as an indicator.

5. Application of the preceding data to the analysis of quicklime.

Following the conclusions derived from the preceding tests, several samples of quicklime were analyzed for calcium oxide. They were all in a fresh state and contained little calcium carbonate.

In each case, approximately one gram of the finely pulverized material was shaken with 150 cc. of a ten per cent. sucrose solution during twenty minutes, the solution filtered and the clear filtrate titrated with standardized hydrochloric acid. At the same time other portions of the same samples were dissolved in hydrochloric acid and the calcium determined in the usual way by precipitation as calcium oxalate. Following are the results:

Sample.	Weight of quicklime taken, grams.	Volume of ten per cent. solution of sucrose taken, cc.	Per cent. CaO by titration method.	Per cent. CaO by gravimetric method.	Variation of volumetric method.
No. 1	1.020	150	92.12	93.00	—0.88
" 2	1.090	150	91.90	92.28	—0.38
" 3	1.006	150	92.15	93.10	—0.95
" 4	1.108	150	95.01	95.90	—0.89
" 5	1.023	150	87.30	87.70	—0.40
" 6	1.232	150	91.70	92.30	—0.60

The results by the sucrose method were in each case slightly lower than by the gravimetric method discrepancy which may be ascribed to a small amount of calcium carbonate present in the sample.

In quicklime which had become partially slaked, this discrepancy would be still greater since the sucrose method would indicate only the actual calcium oxide. Aside from this, the greater ease and rapidity of the latter recommends it in cases where the total calcium is present in the form of the oxide. An entire determination may thus be made in a half-hour with a degree of accuracy quite sufficient for all ordinary purposes.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

A COMPARISON OF METHODS FOR THE DETERMINATION OF STARCH.

BY W. E. STONE.

Received September 1, 1894.

THERE is no longer much doubt among chemists that, in food analysis, the present practice of classifying a large number of widely varying substances under the head of non-nitrogenous extract matter, as an homogeneous material, is wholly erroneous and misleading. The variety of substances covered by this term is well known, and, while it is granted that they are mainly of carbohydrate nature, it is equally clear that, so far as food valuation is concerned, there should be some degree of differentiation between sugars, starches, gums, and the more or less soluble forms of cellulose.

The position of the pentosans in this class of bodies has been pointed out in its different aspects by myself and others at intervals during the past four or five years. It has been shown that these bodies form a distinct constituent of the non-nitrogenous extract matter to a greater or less degree in all fodder articles; that under present analytical methods their individuality as food constituents is wholly merged into that of the more valued carbohydrates; some light has also been thrown upon their digestibility, and analytical methods of a fair degree of accuracy have been devised for their estimation in the presence of other similar bodies.

Mention is made of this instance here to show that really some progress has been made, and that too within a short time, in our knowledge of what, until recently, has been an obscure constituent of the non-nitrogenous extract matter.

The object of this present paper is to call attention along the same line to certain proposed methods for the quantitative estimation of probably the most important of these bodies; *viz.*, starch. At first thought it may appear that the existing methods for the determination of starch are sufficiently satisfactory and accurate; and this is, doubtless, true so far as starch alone is

concerned. But it must be remembered that starch almost always occurs in connection with other soluble non-nitrogenous matters, under which conditions its estimation becomes quite another matter and constitutes exactly the question under discussion. The pentosans or gums are, doubtless, the most common of these accompanying substances and, unfortunately for the analyst, behave toward many analytical methods precisely like starch. Hence, a result which is interpreted to mean starch by a strict adherence to the method, may be due, to a very large degree, to other substances. For example, brewers' grains, which from the very process through which they have passed contain little or no starch, will by the ordinary method of inversion and titration be credited with a large amount of starch. Again, hay or straw yield considerable amounts of reducing sugars on inversion, although they contain a minimum of starch, or even none at all. In both these cases the results are due to the inversion of insoluble gums which are present in large quantities.

With these facts in mind it is apparent that a food analysis should give some information with regard to the relative amounts of these different substances present, and should include determinations of the pentosans, sugars, and starches separately.

In this connection the inquiry arises as to how accurately it is possible to determine these bodies as they occur in connection with each other in the ordinary feeding stuffs, by current and accepted methods. As regards the pentosans and sugars, the state of our knowledge seems far more satisfactory than in the case of the starches, in proof of which proposition the following data are offered.

Five methods of starch determination have been compared upon a variety of materials. Four of the methods involve the inversion of the starch and the estimation of the sugar thus formed by volumetric or optical methods; the fourth method is based upon a combination of the starch with one of the alkaline earths. Following are the details of the different methods:

1. Inversion of the starch with hydrochloric acid and titration with Fehling's solution, known as Sachsse's method: Three to five grams of the starch bearing material are heated in a water-bath with 200 cc. of water and twenty cc. of concentrated acid,

during three hours; the acid is neutralized with soda, the solution filled to 500 cc., and titrated with Fehling's solution in the usual manner.

2. Inversion with nitric acid and polarization, proposed by Guichard, *Bull. Soc. Chim.*, [3,] **7**, 554: Three grams of the material are heated in a water-bath during one hour with 100 cc. of ten per cent. nitric acid, filled to 200 cc. and polarized. The readings are calculated to dextrose.

3. A modification of the preceding: Three grams of material are heated in the water-bath with 100 cc. of a saturated solution of oxalic acid during one hour, the object being to bring the starch into solution. The liquid is cooled and filled to 200 cc. with ten per cent. nitric acid, filtered, and the filtrate heated in the water-bath one hour, attached to an inverted condenser. The solution is then polarized. This method is preferable to the other in that the cellulose and other insoluble substances are removed from the influence of the nitric acid.

4. Inversion of the starch by salicylic acid and polarization, proposed by A. Baudry, *Zeit. f. Spiritus Industrie*, **15**, 41, 42: A normal weight, 5.376 grams is adopted for the Laurent polariscope. This weight, or some multiple of it, is placed in a 200 cc. flask with 100 cc. of water and four-tenths to one-half gram of salicylic acid and heated in a water-bath for thirty minutes; fill to within twenty cc. of the mark with hot water, cool rapidly, clarify by adding a few drops of ammonia, filter and polarize in a 400 mm. tube. The readings on the percentage scale indicate percentages. In our practice, sodium hydroxide was used instead of ammonia for clarifying.

5. Precipitation of the starch from the condition of paste by barium hydroxide, and determination of the excess of the latter by titration with a standard acid, proposed by A. von Asboth, in 1887: One gram of the material, from which the fat has been extracted, is boiled with water to convert the starch into a paste; twenty-five cc. of a solution of barium hydroxide of known strength is run in and the whole allowed to cool; then add 100 cc. of eighty-five per cent. alcohol and fill to 200 cc. A compound of starch is formed containing 19.1 per cent. of barium oxide, which is precipitated by the dilute alcohol. The solution is fil-

tered and the excess of barium hydroxide is determined by titrating aliquot portions with standardized hydrochloric acid, using phenolphthalein as an indicator.

The materials to which these methods were applied included nine different samples, as follows: Pure potato starch, wheat bran, wheat middlings, wheat flour, dried potatoes, corn-meal, hay, cottonseed-meal, and a mixture of starch, sugar, and dextrine. Four of these were samples sent out by the reporter on feeding stuffs of the Association of Official Agricultural Chemists. Before examination, the samples were extracted with water and ether to remove soluble carbohydrates and fats.

The results obtained are best shown by tabulation, as follows:

Materials.	Inversion by HCl.	Inversion by HNO_3.	Inversion by oxalic acid and HNO_3.	Solution by salicylic acid.	Precipitation by $Ba(OH)_2$.
1. Pure potato starch.....	85.75	85.50	85.75	85.47	85.58
2. Dried potato.....	70.92	69.79	68.53		64.25
3. Wheat flour	77.69	70.65	65.29	69.38	59.76
4. Corn-meal	73.24	66.81	70.55		62.11
5. Wheat bran.....	65.86	40.25	38.68		70.77
6. Hay	3.48	19.10	19.10		66.47
7. Wheat middlings.....	30.00	63.09	60.24		60.44
8. Cottonseed-meal	4.15	*	*		54.65
9. Mixture of starch, sugar, and dextrine.....	9.58	21.00	24.08	18.8	33.99

* These solutions were laevorotatory.

From a survey of these data it appears that any of the methods employed, give satisfactory results when dealing with starch alone. It is important to recognize this in order that the responsibility for the discrepancies in connection with the other materials may be properly placed where it belongs; *viz.*, that the variations are due to the complex nature of the materials and not to the method. Allowing for moisture and cellulose, the starch was pure and each method gave credit for the entire amount present. Turning to the other materials the following is to be noted.

1. Inversion by hydrochloric acid. The starch is converted into dextrose and under carefully controlled conditions the reaction is quantitative. Wohl has shown that a very small quantity of acid is efficient in producing complete inversion.

(*Ber. d. chem. Ges.*, **23**, 2084.) According to Märcker, the method of Sachsse here employed gives slightly low results owing to a slight destruction of dextrose by long heating with the acid. This objection does not appear here in comparison with the other methods. There is undoubtedly danger in the other extreme in not heating long enough. The samples numbered 6, 7, 8 and 9 were treated according to the directions sent out by the A. O. A. C. which call for the removal of heat as soon as the starch-iodine reaction disappears. It is possible that under these conditions which are accomplished in a very short time, an appreciable amount of starch does not pass beyond the dextrine stage and escapes detection by Fehling's solution. In this connection it is noticeable that the samples 6, 7, 8 and 9 treated in this way, gave lower results by this than by the other methods.

2. The methods calling for the use of nitric acid seem unusually destructive, yet in the case of pure starch they have given results fairly comparable with the others. As originally proposed by the author, it was feared that the cellulose would be attacked, and the use of oxalic acid as in the third method was proposed. This provides for the solution and removal of the starch by a comparatively mild reagent and this solution is then inverted by the nitric acid apart from the accompanying constituents of the material. The method has a certain advantage of ease and rapidity; the solutions obtained for polarization are also beautifully clear and admit of accurate readings. The effect of the direct action of the acid in the second method is not so marked as might be expected.

3. Both salicylic and benzoic acids completely dissolve starch; the solutions have a right-handed polarization and the degree of rotation is directly proportional to the amount of starch present. The method was originally proposed for the valuation of commercial starches and with such materials is fairly accurate. With feeding stuffs, however, the resulting solutions are frequently too highly colored and opaque to admit of examination in the polarimeter. The method is therefore of very limited application.

5. The use of barium hydroxide as a means of combining and

precipitating starch from solution has attractive features and has been both highly praised and severely criticised. It necessitates the previous removal of all oils from the material. In our hands the results obtained have been somewhat erratic.

One fact is apparent in connection with the above data, if we leave out of consideration the pure starch sample. The results are more or less discordant and in some cases quite unexplainable. For instance, the hay and cottonseed-meal when boiled with water, do not give the iodine reaction for starch, yet each of these special methods for the determination of starch credit them with from four to sixty per cent. of the same. Even fifteen minutes warming with very dilute hydrochloric acid gives an appreciable amount of what we are bound to interpret as starch. This brings us to the inevitable conclusion, that other bodies than starch are present and respond toward each of these reactions in the same way as starch does. We know moreover that the pentosans are such bodies and that they are invariably present to a greater or less degree in materials of the kind under examination.

In order to obtain some experimental data bearing upon the subject, portions of an isolated sample of pentosans were subjected to each of the methods under discussion. The material was, properly speaking, *xylan*, since on inversion it yields only xylose. It was obtained from wheat straw by boiling the same with lime-water and precipitating the xylan with alcohol. It possessed as high a grade of purity as has thus far been attainable in the preparation of these materials. It was free from any other form of carbohydrate and contained about six per cent. of ash materials.

One gram of xylan heated for thirty minutes with fifty cc. of water and four cc. of strong hydrochloric acid was entirely dissolved. The solution was neutralized and made up to 100 cc. Of this 6.7 cc. were required to reduce the copper from ten cc. of Fehling's solution, a result equivalent to 67.16 per cent. of starch.

One gram of xylan was heated with fifty cc. of ten per cent. nitric acid for one hour and became completely dissolved. The solution was made up to 100 cc. and polarized. The reading

was equivalent to that produced by 44.73 per cent. of starch.

One gram of xylan was treated with fifty cc. of a concentrated solution of oxalic acid for one hour by which it became completely dissolved, made up to 100 cc. with ten per cent. nitric acid and heated another hour. The polariscope readings were the same as in the previous case, equivalent to 44.73 per cent. starch.

The salicylic acid method was not applicable.

One gram of xylan was boiled with thirty cc. of water, twenty-five cc. of barium hydroxide solution was added and afterwards thirty-five cc. of eighty-five per cent. alcohol and the whole made up to 100 cc. with water. Upon titration of the excess of barium hydroxide, an equivalent of 47.48 per cent. of starch was indicated.

These results show conclusively that the pentosan which is most characteristic of feeding stuffs and which has been shown to occur in all such materials, behaves, towards the reagents named, in precisely the same manner as starch and in a no less-marked degree. The conclusion is unavoidable that none of the methods for determining starch, based upon the above principles, can be employed with any degree of accuracy upon grains or forage plants or any materials where the presence of these pentosans is probable.

The most hopeful way of avoiding these difficulties would seem to be some method of bringing the starch into solution and removing it from its accompanying carbohydrates without any corresponding influence upon them. One method seems to offer this advantage; *viz.*, the application of diastase or malt infusion to the starch containing material. This method is recommended for use among the European Experiment Stations; it has been shown to yield accurate results with pure starch and can be objected to, if at all, only on account of length of time required and the difficulty of always having a proper preparation of diastase or malt infusion at hand. These are, however, minor objections in the light of greater accuracy secured. The general features of the method are as follows: The weighed material is boiled with water (most effectively under pressure) to convert the starch into a paste; after cooling to 65° C. a small quantity of malt

infusion is added and the temperature maintained at 60° to 65° for a half hour. The starch reaction having disappeared the solution may be filtered off washing the residue thoroughly, the filtrate warmed with a few cc. of acid to complete the conversion into dextrose and finally neutralized, made up to definite volume, and titrated. It remains to be seen what the effect of this process may be upon the pentosans or other similar bodies, concerning which there are few data at hand. I have made some preliminary tests which indicate that these bodies are not affected by diastase. One gram of the xylan, already mentioned, after boiling with water received ten cc. of a fairly strong infusion of malt and was kept at 65° C. for a half hour. At the same time a sample of starch was boiled to a paste, and treated with the malt infusion in the same way. The starch reaction disappeared and the solution reduced Fehling's solution strongly but the xylan did not change the Fehling's solution in the least nor did it appear to have been altered.

It seems, therefore, that in this last method the difficulties presented by the more common methods are to be avoided. The ordinary inversion methods on the other hand furnish no accurate conclusion when applied to the determination of starch contained in vegetable tissues.

For assistance in much of the analytical work cited I am indebted to Mr. D. B. Hoffmann.

NOTES ON THE HARDENING OF MORTAR.[1]

By Wm. P. Mason.

THE following is extracted from the graduating thesis of Mr. J. A. McPherson, of the class of 1894, Rensselaer Polytechnic Institute, the work having been done in my department:

It is common belief among builders, that it is better practice to mix lime mortar and let it lie in a heap some days previous to use, rather than to employ it directly after preparation. In order to test this point, samples of mortar were taken, on successive days, from two separate heaps, of large size; briquettes were made therefrom, and, after an interval of some weeks, were broken for estimation of tensile strength with the following results:

[1] Read at the Brooklyn Meeting, August 16, 1894.

	Days in heap after mixing.	Days exposed to air as a briquette.	Average breaking weight in pounds per square inch.
Mortar No. 1.....	3	50	34.6
" "	4	49	38.6
" "	6	48	38.1
" "	7	46	39.3
Mortar No. 2.....	4	48	36.0
" "	5	47	38.0
" "	6	46	41.2
" "	7	45	41.5

As concerning the formation of calcium silicate through the action of the lime upon the sand, the amount of such formation was found exceedingly small, even after great intervals of time.

After extended experiments with mortar taken from the old Van Rensselaer mansion at Albany, built about 1760, and with mortar from a very ancient tower in the valley of the Lahn, the quantity of calcium silicate found therein was 0.34 per cent. of the total weight of the mortar, an amount altogether too small to be considered as a factor in the hardening of the mortar.

The influence of tempering hydraulic mortar with water containing sugar (one-half pound of sugar to one gallon of water) is shown by the following averages, the mortar used having a tensile strength when tempered with pure water of sixty-three pounds per square inch.

Average tensile strength of sugared briquettes exposed to water during thirty-eight days was 62.75 pounds.

Similar briquettes exposed to air during same period was 65.4 pounds.

There is, therefore, a gain of three and eight-tenths per cent. over the water-tempered mortar in cases where the mortar is used in air, but no advantage when the mortar is intended for subaqueous work.

In South America there has been occasional use of bullocks' blood for tempering hydraulic mortar. In view of this, a number of experiments were made with the same mortar which was used in the sugar experiments, but the tempering was made

with bullocks' blood diluted with one-third its volume of water. The resulting briquettes set somewhat more quickly, and were very hard and firm. Their average tensile strength was:

After exposure to water during thirty-seven days, 68.3 pounds.
" " " air " " " " 69.8 "

Thus showing a gain over the water-tempering of ten per cent. for the briquettes set in air.

RENSSELAER POLYTECHNIC INSTITUTE,
June, 1894.

SOME ALLOYS OF IRON WITH MOLYBDENUM, TUNGSTEN AND CHROMIUM AS SOLUTIONS.

BY JAMES S. DE BENNEVILLE.
Received September 19, 1894.

THE results obtained by the action of silver nitrate on a ferro-tungsten of markedly heterogeneous character appeared to make a study of the reactions of the alloys of iron with the sixth family of interest. In the former paper[1] it was indicated, that a connection existed between the combining ratio of the two constituents and the chemical action of the compound toward reagents. The probable high valency of the iron atom in these metallic compounds, indicated by the fact that all that element appeared to be in combination with the tungsten; the chemical stability of the alloy and the very marked influence of the constituent tungsten on the compounds were noted, as also the nature of the alloy regarded as a solution. The work involved in the present paper is an attempt to broaden the scale of this previous investigation of one compound of a very interesting series. Alloys of the ferro compounds with the tungsten group were examined. The physical properties of these compounds as influencing their chemical properties were noted and the compounds analyzed and their quantitative composition established. The action of the weak solvent, silver nitrate, has been determined as also the reactions of the alloys with liquid and fused solvents. The discussion of the results obtained and their application to these alloys as solutions involved a short summary of the opinions expressed by others on valency and the nature of solution and the intimate connection between that state of matter and alloys.

[1] This JOURNAL, May, 1894.

The alloys were prepared by melting down cast iron with the metals at a white heat in a small Fletcher furnace working with a blast. One hour after reaching a white heat, the cast iron took up the quantity of the second metal indicated in the analyses. The melts were completely liquid and when cold were obtained in the form of buttons weighing twenty-five to thirty grams. The alloys investigated were ferro-molybdenum, ferro-tungsten and ferro-chromium.

FERRO-MOLYBDENUM.

Unalloyed molybdenum is practically infusible in furnaces working with blast. The metal probably could be obtained as a melt in the electric furnace as used by Moissan[1] in his investigations on the reduction by carbon of refractory oxides. As with many other metals of high melting-point, however, its alloys with the more fusible metals can be obtained at a much lower temperature. So with these iron compounds.

The information on these alloys is mainly due to Berthier and Thompson. Berthier states that molybdenum iron alloys are analogous to those with tungsten, a two per cent. molybdenum iron being fusible, very hard, brittle, but tenacious. Billings found that with one per cent. molybdenum, iron became red-short and worthless.[2] Thompson found that iron alloyed with molybdenum more readily than with any other metal. With equal parts of iron and molybdenum the alloy was fusible with the blowpipe. With thirty-three per cent. iron and sixty-seven per cent. molybdenum an alloy of a clear gray-white color was obtained. Twenty per cent. molybdenum iron was whiter than iron, very hard, brittle, tenacious, with granular fracture.[3]

The method of experiment followed was the use of the weak solvent silver nitrate to separate unstable alloys or the metals themselves from the more stable compounds. With the exception of chromium the elements under discussion all react with solution of the silver salt. Dr. Edgar F. Smith has shown[4] that the reaction between metallic molybdenum and the silver

[1] Since this paper was written Mr. Moissan has reduced molybdenum in his electric furnace obtaining the metal as a melt, *i. e.*, fused mass. See *Bull. Soc. Chim.*, [3], 11, 857—5 Sept., *1894*.

[2] Howe, Metallurgy of Steel, p. 86.

[3] Hiorns, Mixed Metals, p. 359.

[4] *Ztschr. anorg. Chem.*, 1, 360.

salt is very exact, silver being reduced to metal and molybdic acid formed. The ratio being Mo : 6Ag. With these iron alloys, the reaction is very complex owing to secondary reactions. The molybdenum is converted into the lower oxide of a blue color. On digesting with the neutral silver salt, no white precipitate of molybdic acid separates.

Separate portions of the alloys were crushed in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then digested with excess of solution of silver nitrate. After twenty-four hours these solutions were decanted and the residue washed by decantation with water. The residue from treatment with neutral silver salt was digested with ammonia. This solution was filtered and added to the first and iron and molybdenum determined. The final residue was treated with nitric acid and, after removal of the silver, molybdenum and iron determined. By this method were obtained: 1. Iron replacing silver. 2. Molybdenum replacing silver. 3. Iron and molybdenum in stable combination.

The quantity of iron extracted by hydrochloric acid was determined. The alloys were not completely decomposed by the acid. A considerable portion of the iron was attacked but the molybdenum would be acted on only to a small extent and would appear in any ratio calculated between total iron and total molybdenum found in the residue. This did not afford a method of separating alloys soluble in the acid solvent.

The experimental results tabulated gave:

Alloy A. Nos. 1–4, close grained crystalline mass showing under the glass segregations marked by a slight yellowish tinge. This sample was fused to a clear button. Brittle, hardness 7, scratching quartz but not topaz. Fracture granular, of a silver-white color, gradually assuming, on exposure to air, a yellowish and in places a brownish tint. Strongly magnetic, not malleable, sp. gr. 8.182.

Alloy B. Nos. 5–12, appearance as with alloy A. strongly magnetic, somewhat malleable,[1] brittle, hardness seven, not so readily oxidized on exposure of fresh fracture to the atmosphere, sp. gr. 7.830

[1] Used relatively. Flattened slightly before crushing.

These alloys slowly decompose water on boiling. The terms "free" iron and "free" molybdenum are used to indicate the iron and molybdenum replacing silver in the silver nitrate. "Free" is used in the same sense throughout the remaining experiments.

I. MOLYBDENUM ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A. Total Fe.	B. Total Mo.	C. "Free" Fe.	D. "Free" Mo.	E. Residual Fe.	F. Residual Mo.	G Ratios A : B	E : F
1 ...	0.6710	0.3290	0.3638	0.0666	0.3072	0.2624	3.50 : 1	2 : 1
2 ...	0.7106	0.2894	0.2608	0.1250	0.4498	0.1644	4.22 : 1	4.70 : 1
3 ...	0.6694	0.3306	0.2162	0.0487	0.4532	0.2819	3.47 : 1	2.75 : 1
4 ...	0.7084	0.2916	0.4932	0.1728	0.2152	0.1188	4.16 : 1	3.15 : 1
5 ...	0.8703	0.1297	0.7185	0.0666	0.1529	0.0620	11.50 : 1	4.23 : 1
6 ...	0.8893	0.1107	0.7154	0.0682	0.1529	0.0635	13.80 : 1	4.13 : 1
7 ...	0.8584	0.1416	0.5706	0.0775	0.2879	0.0640	10.40 : 1	7.73 : 1
8 ...	0.8104	0.1896	0.5328	0.1344	0.2776	0.0552	7.30 : 1	8.63 : 1
9 ...	0.7882	0.2118	0.4634	0.1260	0.3248	0.0858	6.40 : 1	6.40 : 1
10...	0.6670	0.3330	0.4939	0.1612	0.1731	0.1718	3.43 : 1	1.73 : 1
11...	0.8414	0.1586	0.4832	0.0777	0.3582	0.0809	9.10 : 1	7.62 : 1
12...	0.8883	0.1117	0.5406	0.0574	0.3478	0.0542	13.70 : 1	11.10 : 1

Taken for analysis 0.20–0.25 gram.

II. MOLYBDENUM ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

No.	A—13.	B—14.
Iron	0.5982	0.6933
Per cent. of total iron.....	86.74	83.86

Taken for analysis, two grams.

III. MOLYBDENUM ALLOYS, CARBON, SILICON, PHOSPHORUS.

No.	Sample.	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
15.....	Pig iron[1]	2.99	0.37	2.62	2.92	0.33
16.....	Alloy A	2.90	0.17	2.73	0.74	0.31
17.....	Alloy B	2.97	0.20	2.77	0.66	0.30

A third sample was obtained by melting cast iron in the presence of twice its weight of molybdenum. At the heat obtained this was fused down to an irregular mass but a clean button was not obtained. It was very crystalline in structure, the luster in places being of the nature of "parrot" copper ore. The portion unattacked by the weak solvent is of interest, the remainder evidently containing unalloyed molybdenum. The "residual" iron and molybdenum obtained, gave:

[1] Sp. gr., 6.980.

IV. MOLYBDENUM ALLOYS, C.

No.	Residual Fe.	Residual Mo.	Ratio.
18	0.7394	0.2606	4.85 : 1
19	0.4267	0.5733	1.40 : 1
20	0.1320	0.8680	1 : 5
21	0.0770	0.9230	1 : 7

By HCl 42.63 per cent. of total iron dissolved.

In table I the analyses appear to show that the silver nitrate acts not only on unstable alloys but on iron as such or on molybdenum as such. The attacked and unattacked portion varies considerably through the mass. Table IV indicates the influence of mass action. The quantity taken for experiment (0.20–0.25 gram) was small and any marked differentiation would appear. If iron be regarded as limited in its lower compounds by divalency the formula Fe_2Mo (molybdenum being regarded as hexavalent) would represent the saturation-point corresponding to 63.64 per cent. iron and 36.36 per cent. molybdenum. If now the alloy contain less molybdenum than thirty-six per cent., either: 1. The iron in excess must be regarded as present as such in the same sense that water in excess is present in an unsaturated solution, or 2, the alloy is analogous to a cryohydrate, there being present a definite compound or compounds and the excess of the solvent, forming one homogeneous system in its liquid and melted condition, but in the solid (*i. e.* frozen) form making up a system in which the parts bear a definite relation to each other as in cryohydrates, or in which the excess of the solvent is present in a form analogous to ice in such mixtures. 3. That while there may be definite compounds formed in the alloy yet the main bulk of the system is in chemical union, all the iron being united to all the molybdenum no matter how large the quantity of either constituent. 4. That in solution the iron and the molybdenum may be in combination up to the full power of their respective valencies, but that this valency is not exercised (or its power decreases) on cooling, on which the more stable forms of combination appear. Iron or molybdenum in excess may then be present in the solidified alloy and it is not unlikely that owing to the very high melting-point of molybdenum that, as the fusing-point of the mixture rises, a part of the molybdenum exists as a mechan-

ical mixture either never having been in combination with the iron or separating out from the alloy on cooling and the exercise of the more stable valency.[1] The action of a weak solvent, as of any solvent, is mainly dependent on the affinity between the constituents of the compound. That iron and molybdenum form a stable alloy is evidenced by the fact that the action of strong hydrochloric acid fails to decompose these compounds but leaves a residue more or less rich in iron. The silver nitrate can then be regarded as a solvent of a definite compound or compounds in the solidified alloy acting on these and on the metal in excess but failing to attack the more stable compound. Both iron and molybdenum react with the silver salt and the failure of this reaction to take place with considerable percentage of the alloys also points to a strong affinity between the two elements. As with tungsten this is to be expected from the nature of molybdenum as semi-metal. Increased percentage of molybdenum accompanied increased brittleness and decrease in fusibility. The alloys were decomposed by nitric acid which converted the molybdenum to molybdic acid; by potassium bisulphate with evolution of sulphurous anhydride; by fusion with mixture of sodium carbonate and saltpeter; hydrochloric acid left a residue rich in molybdenum.

Analytical Methods.—The direct analysis of these molybdenum alloys (for iron and molybdenum) can be readily made by two methods. 1. The powdered alloy can be fused with oxidizing mixture with addition of caustic soda, cooled and lixivated in water and the soluble sodium molybdate separated by filtration from the residual ferric hydroxide. The molybdenum can then be determined by neutralizing with nitric acid the whole, or an aliquot portion of the solution of alkali molybdate, using methyl-orange as an indicator, and precipitating in the neutral solution as lead molybdate according to Chatard's method.[2] 2. A convenient method of analysis was found by solution in nitric acid. Excess of acid is removed by evaporation and excess of ammonia and ammonium sulphide is then added, digesting in a warm place for at least an hour and acidifying with hydrochloric acid and boil-

[1] Lothar Meyer, Modern Theories of Chemistry, pp. 307, 308.
[2] Fresenius, Quantitative Analysis, p. 353.

ing. Hydrogen sulphide is then passed through the hot solution until saturation. In the indirect analysis (with silver nitrate), after removing silver by hydrochloric acid, it was found necessary to oxidize the boiling solution by nitric acid otherwise the molybdenum remains partly in the form of the lower oxide which does not appear to be readily converted to sulphosalt and on dissolving the iron sulphide in hydrochloric acid the blue color indicates the molybdenum in solution. The precipitated molybdenum trisulphide is oxidized by nitric acid, filtered from any residual sulphur and the cold acid solution precipitated by barium nitrate avoiding an excess. The barium sulphate is filtered off, the filtrate neutralized by ammonia, leaving it barely but distinctly acid, and the molybdenum precipitated as lead molybdate. Throughout these analyses iron is determined volumetrically in sulphuric acid solution by titration with permanganate. A very pure zinc was used for reduction.

Table III explains itself. There appears a decided decrease in the percentage of silicon and a slight increase in the graphitic carbon over the combined. The phosphorus shows no change. The two analyses are only suggestive not indicative of these differences as due to the molybdenum. In determining both phosphorus and silicon the formation of phospho- and silico-molybdate,[1] at least partly soluble, must be taken into account. The graphitic carbon is that determined after treating the iron with hydrochloric acid. In ordinary steels the combined carbon is readily decomposed by the acid and the residue in these irons is probably free from combined carbon. Combustion of the powdered alloy only gave partial results. These alloys slowly decompose water on boiling. Their heterogeneity was apparent on so treating fragments of the alloys, brownish and yellowish spots due to oxidation being scattered over the exposed surface. These were distinct from the iron rust which was also formed. Metallic molybdenum decomposes water on boiling. The richer the alloy in molybdenum the more readily it decomposes water.

FERRO-TUNGSTEN.

The experiments in a former paper[2] on ferro-tungsten were

[1] See under ferro-tungsten.

[2] This JOURNAL, May, 1894.

made on an alloy containing, on averaging twelve analyses, 53 per cent. iron and 46.3 per cent. tungsten and of 10.14 sp. gr.[1] A second alloy of eighteen per cent. tungsten was made. The method of preparation and experimentation followed was the same as with the molybdenum compounds. The action of tungsten on silver nitrate has been found by Smith[2] to be analogous to that of molybdenum. Tungstic acid is formed and silver reduced to metal, the ratio being W : 6Ag.

In the alloy previously described (Nos. 22–26) it was found that the iron and tungsten were present in a very stable form, only a small percentage of tungsten and iron being attacked by the silver solution. In view of the more extended experiments this soluble portion can be regarded as a part of the alloy more readily attacked than the residue. Schneider separated from a high tungsten iron what appeared to be two alloys, one magnetic and the other non-magnetic corresponding to the formulas Fe_3W and Fe_6W. He used hydrochloric acid as a means of separation from the soluble iron.[3] It must be taken into consideration, however, that tungsten is but little attacked by hydrochloric acid and in the case of an alloy of which the iron was readily attacked by acid it would be left in the residue and vitiate any ratio calculated from analysis of that residue. With silver nitrate, however, there is a definite reaction between the silver and the constituents of the alloy. They both act on it, although (and the varying ratios point to the latter alternative) the doubt exists as to whether the silver salt attacks a definite compound or varying quantities of alloys of different composition. The chemical inertness of these alloys is much more conspicuous than with the molybdenum compounds. Whatever compounds are formed in these alloys, are probably compounds made up of atomic linking and not the union of like molecules. These compounds are formed from a solution, and Heycock and Neville on determining the molecular weights of metals dissolved in sodium found for copper, silver, lead, antimony, zinc, cadmium and mercury, one atom in the molecule. Ramsay obtained like results by

[1] I am indebted to Dr. Wm. H. Wahl through Mr. F. Lynwood Garrison for this alloy.

[2] I am indebted to Dr. Smith in a private communication for reactions of molybdenum and tungsten bearing on these alloys. See *Ztschr. anorg. Chem.*, 1, 360.

[3] Howe, Metallurgy of Steel, p. 81.

determination of the variation of vapor tension of mercury.[1]

Analytical Methods.—The best method for direct analysis of these compounds was found to be fusion with the oxidizing mixture with addition of caustic soda and lixiviation in water. The soluble sodium tungstate was filtered from the residual ferric hydroxide and the tungsten precipitated in neutral solution by mercurous nitrate according to the method of Wolcott Gibbs.[2] In the indirect analysis, to the solution obtained on filtering from the unattacked residue, ammonia in excess was added and then ammonium sulphide. After digesting in a warm place for an hour this solution was acidified by hydrochloric acid and boiled. Hydrogen sulphide was then passed through it to saturation and the precipitate of silver sulphide and tungsten trisulphide filtered off and tungsten separated from silver by solution in ammonium sulphide. After removal of ammonium salts and oxidation, tungsten was determined as tungstic oxide, WO_3. The unattacked residue, after removal of silver,[3] was fused with oxidizing mixture and the sodium tungstate separated from the residual ferric hydroxide by lixiviation in water and filtration.

The experimental results gave:

Alloy D, Nos. 22–26.[4] Crystalline with marked differentiation throughout the mass showing a number of cleavage planes of a pyritous appearance, also lining the cavities. The body or cementing portion of the alloy being finely crystalline but without the luster of the molybdenum compounds. Hard, brittle and tough. Sp. gr. 10.14. Alloy E, Nos. 26–29. Fine-grained crystalline mass without visible differentiation. Color, dark gray, the original pig iron being lighter in color. Brittle. Hardness barely 7. Sp. gr. 7.935. This alloy scratched glass readily; quartz only with difficulty. On boiling in water and subsequent oxidation this alloy showed patches of brown, yellow and bluish spots distinct from the iron "rust" formed.

[1] Mendelejeff, Principles of Chemistry, 1, 123. Ramsay obtained with barium, calcium, and potassium abnormal results, the number representing the first two metals being one-half the atomic weights. With potassium a number considerably less than its atomic weight was obtained.—*J. Chem. Soc. Trans.*, *1889*, 521.

[2] Blair, Chemical Analysis of Iron, p. 123. Modified as described in Classen (trans. of Smith) p. 174.

[3] This residue was not attacked by dilute nitric acid.

[4] As described by Dr. Wahl.

These oxidation-points were distributed all through the mass with considerable uniformity.

V. TUNGSTEN ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A. Total Fe.	B. Total W.	C. "Free" Fe.	D. "Free" W.	E. Residual Fe.	F. Residual W.	G. Ratios A : B.	Ratios E : F.
22..	0.5166	0.4834	0.0122	0.0403	0.5044	0.4431	3.51 : 1	3.74 : 1
23..	0.4109	0.5891	0.0283	0.0526	0.3826	0.5365	2.30 : 1	2.34 : 1
24..	0.5276	0.4724	0.0566	0.0370	0.4709	0.4355	3.66 : 1	3.54 : 1
25..	0.5270	0.4730	0.3156	0.0632	0.2093	0.5881	3.66 : 1	1.17 : 1
26..	0.5265	0.4735	0.0152	0.0541	0.5096	0.4211	3.66 : 1	4 : 1
27..	0.8053	0.1947	0.7104	0.0652	0.0949	0.1295	13.6 : 1	4.17 : 1
28..	0.8119	0.1881	0.7111	0.0760	0.1008	0.1121	14.1 : 1	3.4 : 1
29..	0.8124	0.1876	0.6980	0.0721	0.1144	0.1155	14.2 : 1	3.15 : 1
30..	0.8584	0.1416	0.7393	0.0331	0.1221	0.1055	20 : 1	2.6 : 1

Taken for analysis, 0.20–0.25 gram.

VI. TUNGSTEN ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

No.	D-31.	E-32.
Iron	0.3728	0.6223
Per cent. of total iron	70.34	75.70

Taken for analysis, two grams.

VII. TUNGSTEN ALLOYS, CARBON, SILICON, PHOSPHORUS.

No.	Sample.	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
33	Alloy D[1]	2.40	1.84	0.56	2.07	0.25
34	Pig iron[2]	3.06	0.77	2.29	3.30	0.32

These alloys also are marked by heterogeneity, containing more and less stable compounds. Their crystalline character is more prominent than with the molybdenum compounds, cavities in the alloys being lined with imperfect crystals by no means microscopic and showing cleavage planes of a pyritous appearance. Poleck and Grützner[3] have examined one of these forms in a ferro-tungsten. Their description of the alloy is of a crystalline mass, dense and hard, of a steelish gray color, metallic luster, with cavities lined with small crystals, found by Hintze to be of the hexagonal system or possibly rhombohedral if hemihedral in form. They were nearly as hard as corundum and were completely attacked by sodium potassium carbonate, giving the formula FeW_2 analogous to FeS_2. The cementing material

[1] Made from tungsten and pig iron, No. 34.

[2] Sp. gr., 7.146.

[3] Abstracted *Bull. Soc. Chim.*, No. 8, *1893*.

gave the formula Fe_3W_3C, and was nearly as hard as the crystals. Density 12.92–13.14. F. N. Riddle[1] smelted Lake Superior hematite with tungstic oxide and carbon. In the crystalline mass were obtained steel-gray crystals insoluble in hydrochloric acid and found to contain 98–99.5 per cent. tungsten. Density 15–16. With nickel he states the separation of this crystalline tungsten was still more marked. The variation of results among different observers shows the influence the conditions of preparation have on alloys of iron and tungsten.

The chemical reactions of these tungsten alloys strongly indicated the influence of the tungsten. Acid solvents were practically useless as a means of analysis. Both nitric acid and aqua regia decompose them but very slowly and only by removing the protecting coating, the yellow hydroxide $Wo(OH)_2$, and adding fresh acid. Potassium bisulphate (sulphuric acid at a red heat) decomposes them with evolution of sulphurous anhydride. An oxidizing mixture of sodium carbonate and saltpeter was a complete and ready means of decomposition, as also was caustic soda. Hydrochloric acid acts only partially on the iron. These reactions are those of metallic tungsten and indicate a combination of iron and tungsten equally inert.

The formation of phosphotungstate and silicotungstate, partly, at least, insoluble and remaining with the tungstic acid, necessitated some modification in the determination of these elements. The separation was made by fusing the powdered alloy with oxidizing mixture and caustic soda dissolving the melt and filtering from the residue. This residue was treated in the usual manner for silicon. To the solution containing alkali tungstate, silicate (in part), and phosphate, enough ferric chloride is added to precipitate silicic and phosphoric acid. The solution is now acidified, the ferric carbonate formed dissolving. Carbon dioxid is expelled by boiling, and ammonia in excess added to re-solution of precipitated tungstic acid. Silicic and phosphoric acids are now determined as usual. In determining arsenic and phosphorus in pig copper this method was found to be accurate, these elements going with iron in preference to lead, antimony, tin, or bismuth.[2]

[1] *Am. J. Sci.*, *1889*, [3], **38**, 160.

[2] Modification of a method described in Crookes' Select Chemical Methods, p. 430.

FERRO-CHROMIUM.

Since the publication in 1820 by Berthier[1] of his experiments on alloys of chromium with iron, these compounds have been carefully studied both from a chemical and physical standpoint with regard to their metallurgical application. Physically, chromium increases the hardness and tensile strength of iron, but makes it brittle. As noted in the discussion of ferro-molybdenum the properties of hardness and density appear to be connected with condensation, and in the case of both these properties they increase with the content of chromium. Brustlein[2] notes that the carbon increases with the chromium, giving a series from twelve per cent. chromium, two per cent. carbon to eighty per cent. chromium with eleven per cent. carbon. Howe[3] also notes this increase of the carbon content and also that, as in the case of manganese, the chromium prevents the separation of graphitic carbon. According to the same authority chromium combines with iron "in all proportions or at least up to eighty per cent." the alloys being markedly heterogeneous in nature, samples from the same piece giving very different results when subjected to physical tests. He etched a plate of chrome steel with sulphuric acid and noted in it the presence of portions not attacked by the acid and which he considered probably to be alloys rich in chromium. The analyses made for this paper give the same results in regard to heterogeneity in these chromium alloys and in the other alloys examined and show the necessity of taking from half to one gram of an average for analysis. The experimental method pursued was the same as with the molybdenum and tungsten alloys. Nitric acid, dilute or concentrated, does not attack metallic chromium. The silver nitrate would not, therefore, attack the chromium constituent of these alloys. The action of the reagent, however, is of interest as showing the amount of iron in stable combination and the figures so obtained are given. The chromium alloys of iron show the influence of the chromium in almost as positive a manner as with tungsten compounds. Acid solvents act very slowly on high chrome alloys. Potassium bisulphate and the oxidizing mixture decompose them

[1] *Annalés des Mines*, [1] 6, 573.
[2] Hiorns, Mixed Metals, p. 359.
[3] Howe, Metallurgy of Steel, p. 75.

readily, and the latter energetically, the oxidation of the fine powder giving rise to a considerable evolution of heat which rapidly raises the crucible to bright redness; only one alloy was made.

Alloy F. Brilliantly crystalline; acicular, with a cleavage appearance like antimony. Brittle. Scratches glass with difficulty. Does not scratch quartz. Specific gravity, 7.464. Hydrochloric acid decomposed this alloy.

VIII. CHROMIUM ALLOY WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

	A	B	C	D	E Residual	
	Total	Total	"Free"	Residual	per cent. total	Ratio
No.	Fe.	Cr.	Fe.	Fe.	Fe.	A:B.
35.....	0.8706	0.0794	0.4832	0.3874	44.49	10:1
36.....	0.8684	0.0804	0.4497	0.4187	48.21	10:1
37.....	0.8481	0.0999	0.4770	0.3711	43.75	8:1
38.....	0.9154	0.0360	0.5092	0.4062	44.37	24:1

Taken for analysis 0.20–0.25 gram.

IX. CHROMIUM ALLOY, CARBON, SILICON, PHOSPHORUS.

No.	Sample	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
40	Alloy F.....	2.46	1.64	0.82	3.37	0.29
41	Pig iron	3.06	0.77	2.29	3.30	0.32

No. 40 was made by melting No. 41 with ninety per cent. ferrochrome.

Analytical Method.—In direct analysis for determination of chromium and iron the fusion with oxidizing mixture was adopted and separation of the chromate from ferric hydroxide effected by filtration. In determining iron and chromium digested with silver salt, the insoluble residue was dissolved in aqua regia, the silver chloride filtered off and the solution made alkaline by sodium hydroxide, boiled and bromine added. The residue of ferric hydroxide was filtered from the chromate. In the acid filtrate the chromic acid was reduced by hydrogen sulphide and the boiling solution precipitated by ammonia. Adhering alkali, forming chromate on ignition, was tested for by mercurous nitrate.[1]

GENERAL CONSIDERATIONS.

In connecting solutions and alloys the part that the metal in excess plays is that of water in aqueous solutions of salts. That

[1] A Method used for chromite analysis by Dr. F. A. Genth.

this is not a purely mechanical part but that a distinct force is acting between the components of a solution is evident from the modification both of solvent and of the dissolved substance. The physical state of the latter changes, probably assuming the liquid form,[1] and the specific gravity, refractive power, tension of vapor, boiling and freezing-points,[2] are affected often considerably. The thermic effect resulting in evolution or absorption of heat, and alteration in volume[3] shown by contraction or expansion, further indicate chemical action. The combination is an indefinite one in so far as addition of the solvent is concerned; but the amount of dissolved substance is strictly limited by temperature and pressure (in the case of gases). Van 't Hoff[4] has intimately connected gases and solutions comparing diffusion to evaporation and solution to vaporization. His experiments on osmotic pressure, showing that solutions obeyed the laws of gases and that Avogadro's law could be applied to them.

The formation of definite compounds in solution is well established, the halogen acids and nitric acid affording examples of solutions of constant boiling-point; and until that concentration is reached the products of evaporation are mainly water or, as the case may be, acid.[5] The cryohydrates are also examples of this definite combination, and such substances as $H_2SO_4H_2O$ and salts with water of crystallization. Although these very definite compounds are formed with water, solution itself is a homogeneous system[6] and the existence of these compounds as such in the fluid cannot be asserted. Sterry Hunt, who considers solution as the type of chemical action in its "identification of the different," regards the state as one in which all definiteness is lost and in which we cannot assert the existence of any one compound, or even element, more than another.[7] We can only possibly predict what, under altered conditions, we can obtain from it.[8] He sums up the theory of solution as "the formation of

[1] Mendelejeff, Principles of Chemistry, 1, 70.

[2] Ibid, 1, 86, 87.

[3] Lothar Meyer, Modern Theories of Chemistry, 466, 481.

[4] *Trans. Swedish Acad. Sciences*, Part 21, No. 17, *1886;* quoted by Mendelejeff, 1, 64, 65. See translation by Ramsay, *Phil. Mag.*, 26, 81, *1888*, from *Ztschr. phys. Chem.*

[5] Ostwald, Solutions, p. 9, trans. by Muir.

[6] Ibid, p. 148.

[7] New Basis of Chemistry, p. 22. [8] Ibid, p. 10.

definite compounds with water accompanied with all the phenomena of chemical union," further addition of water giving rise either to decomposition and formation of new compounds or to admixture of "one definite solution or liquid species with another less dense solution, or with water." These compounds "being separable in a solid state by change of temperature or in a liquid state (theoretically) by gravity;" liquidity is but an accident of solution, depending on temperature and pressure.[1] Arrhenius from his investigations of the depression of the freezing-points and lowering of the vapor pressure of solutions of electrolytes came to the conclusion that the system was one of dissociation.[2] Mendelejeff bringing all such compounds as solutions, cryohydrates, colloids, and amorphous silicates, under the law of definite and multiple proportions regards solutions as fluid unstable definite chemical compounds in a state of dissociation.[3]

Alloys, with the exception of some of the amalgams, are solids at the ordinary temperature and require a more or less elevated degree of heat for fusion, their melting-point depending on that of their constituents and on the nature of the alloy. As solutions, therefore, they only exist at high temperatures and it is at those temperatures that the laws of solutions must be applied to them. As is the case with liquids, they may be saturated or unsaturated compounds, in the latter case one of the constituents being present in excess and acting as the solvent, *i. e.*, corresponding to the part excess of water plays in the solution of a salt. If the solution be regarded as a state of dissociation, then while the mass of the alloy is in the liquid state (fused) we have a homogeneous system, and two elements may be in unstable combination which on cooling, *i. e.*, solidifying or freezing, separate in definite compounds limited by the valency of the constituents, any excess of one of the elements being indicated by the presence of that element in an uncombined state. When, therefore, there is no excess indicated in an alloy of one constituent over another it can be justly assumed that all is in combination, and the presence of an excess of one of the metals

[1] Systematic Mineralogy, pp. 77, 78, 82.
[2] Ostwald, Solutions, pp. 189, 214. Trans. of Muir.
[3] Mendelejeff, Principles of Chemistry, 1, 105.

would correspond to the ice present when an aqueous solution of a salt is cooled below its freezing-point, or to those compounds of salts with much water known as cryohydrates. The freezing-points of metals and their alloys, with a few exceptions, are much higher than the normal temperature, 15° C. In his study of the solution of liquids in liquids W. T. Alexeef found that two liquids mutually soluble, intermix in all proportions at certain temperatures. At lower temperatures the solubility is limited, finally reaching a minimum.[1] This may be and probably is the case with melted metals, but the condition in which we can observe and examine them corresponds, as said before, to the frozen state.[2] Hardness and indifference to chemical reagents have long been associated with condensation, increased density being generally associated with these properties and indicating complexity of structure advancing from the gaseous to the solid form.[3] In liquids, although friction appears as a factor, yet there is free communication within the bounds of the liquid; a considerable condensation, however, takes place. In the conversion of steam, gaseous H_2O, to water and ice, Sterry Hunt found this condensation to be for water, 1192 H_2O, and for ice, 1094 H_2O,[4] and in mineral species increased density was found to be associated with hardness and chemical indifference.[5] Ramsay in determining the molecular formulas of liquids by means of their molecular surface energy, found that condensation increased with fall in temperature and obtained for sulphuric acid of 1.82 sp. gr. the very complex formula not lower than $(H_2SO_4)_{22}$ at ordinary temperatures.[6]

Regarding alloys as solutions, many of their physical properties can be explained. The alloy changes its nature both physical and chemical, differing from its constituents in volume (*i. e.* density) and melting-point, and forming often definite molecular compounds. This modification of its properties is greater or

[1] Mendelejeff, Principles of Chemistry, 1, 74, and Ostwald, Solutions, p. 40, trans. of Muir.

[2] Ibid. 1, 105.

[3] Sterry Hunt, Systematic Mineralogy, p. 86, seq.

[4] New Basis of Chemistry, p. 109.

[5] Researches of J. B. Mackintosh, *J. Anal. Chem.*, 1, 10. Sterry Hunt, Systematic Mineralogy, p. 93.

[6] *J. Chem. Soc.*, 63, 1089, Sept. *1893*. 65, 167, March, *1894*.

less according as the constituents are separated in their nature. Mendelejeff cites the series formed by sodium with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc, changing its properties from the distinctly saline sodium chloride to the sodium zincide and with this change in properties as the union is with the element more and more like in nature to sodium increasing in valency; but they are distinct and definite compounds and not to be distinguished on the ground of chemical nature. He notes the same properties in the union of metallic oxides, instancing the large number of complex aluminum silicates in which the two constituents are very like in nature acting as feeble base or feeble acid, and united in such a substance as lava glass in varied proportions giving on crystallization definite compounds, the silicates.[1] The analogy between these vitreous substances, with their microcrystalline structure, and alloys is a striking one.

The question of variable valency of the elements arises in these compounds of like elements. Are they to be regarded in the same light as with those of rigidly defined proportions with unlike elements? This is evidently the case. Definite crystallized compounds of alloys are known, with well-defined properties unlike those of either of the constituents. The alloys $SnCu_3$ and $SnCu_4$, as also $PbSn_4$, are examples. Polymerism has also its analogue in allotropism.[2] But in the union between unlike elements this variability appears. Sodium forms several oxides, as likewise gold, silver, copper, etc. The elements under consideration, chromium, molybdenum, and tungsten, unite with oxygen in several ratios. These latter are especially interesting in their relation to the silicates. The complexity of their silico-compounds and phospho-compounds, was long ago established by Wolcott Gibbs[3] and if this complexity is related to the union of like properties in these oxides the same complexity is to be expected in the union of elements of like nature—as these metals. These alloys in the melted state are solutions, as the melted lava glass is a solution. There is a homogeneous system

[1] Mendelejeff, Principles of Chemistry, I, 111,112. See Matthiessens Conclusions, *Brit. Ass. Reports, 1863*, p. 97, cited in Fownes' Chemistry, p. 290.

[2] Ernest Meyer, History of Chemistry, pp. 377, 454.

[3] Gibbs, *Am. J. Sci.*, [3], 14, 61.

the equilibrium of which is disturbed on cooling and at different temperatures different salts crystallize out. These salts may represent combinations of the atoms as truly as NaCl or they may be molecular compounds of a salt with the solvent metal, *i. e.*, present in definite proportion analogous to water of crystallization as in the salt $Na_2CO_3, 10H_2O$. The number of such compounds separating out during the slow cooling of an alloy may be, and probably is, very great. In many alloys with slow cooling, a macrocrystalline structure often results, but with rapid cooling the result is the microcrystalline form. This is of such importance that the commercial use of many alloys requires their rapid cooling, from their tendency to coarsely crystalline structure and consequent loss of homogeneity. That the valency of an element is related to its electro-chemical behavior has been shown and the value of an element increases toward like elements and decreases or concentrates itself in union with unlike elements, *i. e.* "Elements of variable valency exercise the smaller valency when combining with those for which they have the greater affinity but the higher valency when uniting with those for which they have but small affinity.[1] The possibility of self-saturation must be taken into account[2] and valency established on indirect determination is doubtful. In these compounds or alloys the question of valency becomes a very difficult one. The quantitative composition of a well-developed individual, such as a crystal, is no guide in itself to the valency of the constituents as crystallization is essentially molecular. We know that the passage from gas to liquid and to solid involves a condensation and most frequently a very great condensation of volume, and experiment on the solutions of metals in mercury and in sodium show many of them to be monatomic; therefore, while the molecule itself may contain but a comparatively small number of atoms, the union of these simple molecules to form larger ones brings about great complexity of structure indicated by the increased density, hardness, and chemical inertia. If this is the case the molecule of these ferro-compounds must be very complex and assuming the simplest formulas from the

[1] Lothar Meyer, Modern Theories of Chemistry, p. 349.

[2] Ibid on valency, p. 307 seq.

analyses—which, while representing the average of a number of alloys in the solid state, can be carried back to the liquid state when the system was homogeneous—very large integral weights or equivalents are obtained. The valency of iron to tungsten is at least equal to its valency to chlorine or to oxygen, and these are only minima. Ruthenium and osmium have been shown to be at least octovalent, and if the ammonia (NH_3) in the ammonium cobalt salts be considered as atomic and not molecular, cobalt, a metal closely allied to iron, must be accepted as dodecavalent.[1] The ratios obtained in column G of the tables do not afford an indication of the value of the iron atom in these alloys. The ratio E : F of the residues give for the highest formulas $Fe_{11}Mo$ and Fe_4W, but unquestionably represent mixtures.[2] The presence of an allotropic form of iron, β iron, as taught by Prof. Osmond, is also to be taken into account. These elements of the sixth family, tungsten and chromium, come under the list of β forming elements. As far as the solution of steels in acids or in the copper alkali salt, this β or hard "adamantine" form of iron appears to act as other modifications. There is no reason to believe it would act differently with silver nitrate.[3] The influence of mass appears in the increased ratio of the predominant metal in E : F. This is not so marked in the case of tungsten. A considerable uniformity runs through the analyses but several numbers (as I, 8, 9, 10) evidently mark points of segregation.[4]

[1] Lothar Meyer, Modern Theories of Chemistry, pp. 347, 348.

[2] The silicides and phosphides of iron are very inert. A ferro-silicon containing fifteen per cent. silicon was insoluble in nitric or hydrochloric acid, but soluble in aqua regia.

[3] Prof. Osmond in his paper (*J. Iron and Steel Inst.*, p. 38, *1890*) ascribes the power of retaining at the normal temperature iron in this β or hard form, to a number of elements among them tungsten and chromium; the hardness of such iron being due not only to the mechanical strains set up in the solid on cooling but to molecular strains, perhaps due to osmotic pressure exerted by elements of small atomic volume (discussion of Prof. J. O. Arnold's paper, May, *1893*). Prof. Arnold considers the hardening property as due to mechanical strains on cooling probably caused by the formation of definite compounds such as Fe_3C. These authorities do not appear to regard as worthy of notice the theory that all the carbon, phosphorus, silicon, etc., is uniformly distributed through the iron and in combination with it; and in view of the small quantities of such elements present such a view appears chemically untenable. I am indebted to Mr. Garrison, who kindly brought these papers to my attention and placed them at my disposal for consultation.

[4] In the action of silver nitrate on these alloys there is a considerable evolution of heat. This is also the case with iron.

That the melting-point of alloys is not the mean of the melting-points of their constituents but is influenced by properties probably chemical, is well known. An example of this is afforded by platinum which is only fusible by the oxyhydrogen flame in a lime furnace, but which with iron forms a readily fusible alloy at the highest temperature of the blast-furnace and also with a number of other elements, alloys fusible at the heat of the Bunsen lamp. This lowering of temperature is found with other still more infusible elements of this group; *viz.*, palladium, iridium, ruthenium, and osmium.[1] Tungsten, molybdenum, and chromium, form a group of very infusible substances but these iron alloys are formed readily at the temperature of the blast-furnace. Hardness, chemical indifference, and density are associated with molecular complexity and the tungsten group in their metallic forms are probably represented by formulas expressing great condensation and affinity between the like atoms. The formation of these iron alloys, therefore, must be preceded by a breaking up of this union between like atoms and molecules and this is brought about by a state of solution. The affinity of iron and the sixth family is then greater than the affinity of the like atoms, for on cooling from the homogeneous system of solution stable alloys of iron and the second constituent separate out. Now, as before cited, Heycock and Neville found (confirmed by Ramsay) that on determining the molecular weights of the metals dissolved in sodium and in mercury the results gave one atom in the molecule for a large number of metals, indicating that in solution in metals, a state of dissociation exists analogous to that of the aqueous solution. If this holds good, therefore, for these iron compounds, that in the liquid or melted condition the complex molecule of iron and tungsten existing in the solid state is broken up into a simpler form, then the affinity between the constituents of these alloys can act. The investigators found that on dissolving the metals in atomic proportions in molten tin on applying Raoult's method[2] to the lowering of temperature of solidification a constant was obtained, this being in accordance with Coppet's law

[1] Howe, Metallurgy of Steel, p. 79. A. Joly., *Compt. rend.*, *1893*, 116, 430, on melting-point of the platinum metals.

[2] See *Am. Chem. J.*, 11, 67, 72.

that "solutions whose contents are in the ratio of the molecular weights of the dissolved salts freeze at nearly the same temperature.[1]" That is, the freezing-point is a function of the molecular weight. Indium and aluminum gave abnormal results indicating a more complex molecule in solution.

Chemical action is also indicated by change in volume and in his researches on dilute solutions Ostwald determined the amount of chemical change—in this case representing the avidity of the acids—by the contraction or expansion of the liquid.[2] With alloys, the same phenomena is observed. As a rule with the formation of definite compounds, *i. e.*, on cooling, contraction ensues. Alloys of bismuth, however, expand being analogous in this respect to ice. These iron alloys show change in volume, indicating by their increased density that with them a contraction has taken place. In every case there is a marked increase in specific gravity. Comparing the specific gravities:

X. TABLE ON COMPARATIVE DENSITIES.

Nos.	Samples.	Sp. gr. of metal.	Sp. gr. of alloy.	Composition.	Sp. gr. of pig iron.	From composition. difference.	Equivalent weights.
1–4	A.....	Mo=8.6	8.182	Fe_4Mo	6.980	+0.88	175052
5–12	B.....		7.830	Fe_8Mo	6.980	+0.67	167562
22–26	D	W=19.2	10.140	Fe_7W_2			216996
27–30	E.....		7.935	$Fe_{16}W$	7.146	+0.08	169809
35–38	F.....	Cr=6.8	7.446	$Fe_{20}Cr_3$	7.146	+0.27	159629

Fe here represents the complex compound containing phosphorus, silicon, and carbon—pig iron. The sign—minus is to be expected with chromium. If these alloys are to be considered as chemical compounds and as atoms bound together into molecules and these molecules into still more complex molecules then these composition formulas, can be taken as representing the simplest average composition of the definite compounds in the alloy in the solid state. There may be and certainly are compounds in these alloys represented by formulas more complex than these simple formulas, for the elements, carbon, silicon, etc., have not been taken into account. Assuming these latter, however, column VI gives the equivalent weights $H_2O = 21400$.

[1] *J. Chem. Soc. Trans.*, *1889*, 666, *1890*, 376. Ramsay, Ibid, *1889*, 521. Quoted in Ostwald, Solutions, p. 231, by Muir.

[2] Lothar Meyer, Modern Theories of Chemistry, p. 481 seq.

These high equivalents explain the physical properties, such as hardness and density, and the chemical inertia of these compounds.[1]

In this connection it should be noted that there is a difference in density in a metal as solid and when in the melted condition. Wrightson[2] in his experiments on the relative specific gravity of cast iron in the two states found that the maximum volume was obtained on passing from the liquid to the solid. The same result was obtained from experiments made on melting solid iron or on cooling molten iron to solid. In the latter case there was observed: first an expansion, followed by contraction and again by expansion. The observed differences were small. Henri Moissan in his experiments on carbon dissolved in iron made use of this change of volume of the iron to subject the carbon, on sudden cooling, to great pressure.[3]

From these results it can be concluded:

1. That these alloys by their resistance to chemical reagents, their hardness and increased specific gravity, indicate a chemical union between the constituents. That in these alloys there are present a number of compounds, some of which are more stable than others, the latter being readily attacked by weak solvents. That these compounds are distributed with considerable uniformity throughout the mass of the alloy, segregation being the exception, not the rule, and that their freezing-points must be approximately the same, preventing the segregation of alloys of great density in any one portion of the alloys; that the more stable of these alloys are definite chemical compounds; that the less stable may be definite compounds or of the nature of cryohydrates or with one of the constituents present in the mixture in a state analogous to that of ice in a frozen salt solution in which water is in excess.

2. That, therefore, in these alloys the existence of definite compounds differing in their action toward solvents; their contraction as indicated by their specific gravity, hardness, etc., the fact that chemical union exists involving the breaking up of the

[1] Sterry Hunt, New Basis of Chemistry, p. 51 seq. and 100. Systematic Mineralogy, p. 86.

[2] Howe, Metallurgy of Steel, p. 254.

[3] *Bull. Soc. Chim.*, 11, 8, January, *1893*.

complex iron, molybdenum, tungsten, and chromium molecules and their union to form a new compound, *i. e.*, the passing of a heterogeneous system of molecules of like elements to a homogeneous system in the melted condition and again to a heterogeneous system in the resultant alloy; that these properties indicate a condition in these alloys analogous to an aqueous solution of a salt converted by cold to the solid state.

3. The high melting-point of the element in combination with the iron and its chemical affinity for iron is especially favorable to the separation of alloys from the cooling solution, and is the cause of the heterogeneity of these compounds. This separation of salts, *i. e.*, segregation, draws the analogy between these alloys and solutions closely.

XI. COMPOSITION OF ALLOYS.

Alloys.	A.	B.	C.	D.	E.
Molybdenum.....	0.2979	0.1665			
Tungsten.....			0.4646	0.1696	
Chromium					0.0702
Iron.....	0.6626	0.7942	0.5251	0.7832	0.8799
Phosphorus	0.0031	0.0030	0.0004	0.0025	0.0029
Silicon	0.0074	0.0066	0.0014	0.0207	0.0337
Combined carbon...	0.0017	0.0020	0.0075	0.0184	0.0041
Graphitic carbon...	0.0273	0.0277		0.0056	0.0082

THE PROTEIDS OF THE KIDNEY BEAN.

(PHASEOLUS VULGARIS.)

BY THOMAS B. OSBORNE.

(*Continued from page 712.*)

Another trial was made by treating 400 grams of bean-meal, previously exhausted by benzine, with one per cent. sodium chloride solution, dialyzing the extract for twenty-four hours, and filtering off the precipitated phaseolin. The clear filtrate after standing over night, deposited a considerable quantity of proteid, but the solution with this deposit was returned to the dialyzer and left for two days longer, when it was filtered, the precipitate washed with water, alcohol, and ether, dried over sulphuric acid, and six grams of preparation 36 obtained.

PHASELIN, PREPARATION 36.

		Ash-free.
Carbon	50.44	51.41
Hydrogen	7.14	7.28
Nitrogen	14.31	14.59
Sulphur	0.46	0.47
Oxygen		26.25
Ash	1.94	
		100.00

The filtrate from preparation 36 was then dialyzed into distilled water which was renewed every twenty-four hours for several days. After a week the solution was filtered and the precipitate washed with water, alcohol, and ether, and dried over sulphuric acid. It weighed 1.60 grams, 37.

PHASELIN, PREPARATION 37.

	I.	II.	Average.	Ash-free.
Carbon	51.38	51.22	51.30	52.19
Hydrogen	7.25	6.99	7.12	7.24
Nitrogen	14.52		14.52	14.79
Sulphur } Oxygen }				25.78
Ash	1.83	1.61	1.72	
				100.00

One more preparation, 38, was made in the same manner as 37, and had the following composition:

PHASELIN, PREPARATION 38.

		Ash-free.
Carbon	50.20	51.27
Hydrogen	7.07	7.22
Nitrogen	14.02	14.32
Sulphur	0.50	0.51
Oxygen		26.68
Ash	2.06	
		100.00

Further dialysis in distilled water, of the filtrate from preparation 37, gave no more precipitate. The solution was therefore saturated with ammoniun sulphate, and the precipitate so produced filtered off and dissolved in distilled water. This solution which now had a volume of about 400 cc. was dialyzed for some

days, first in river water, and afterwards in distilled water, but only a trace of substance separated. This was filtered off, and the perfectly clear solution gave the following reactions:

Saturation with sodium chloride produced no precipitate until acetic acid was added. Acetic acid in the absence of salt gave no precipitate. Nitric acid gave a turbidity when added in considerable quantity, and the addition of some sodium chloride produced no further precipitation. Copper sulphate gave no precipitate. This solution when heated became turbid at 57° and particulate at 63°.

The entire solution was therefore heated to 70° in a water-bath which did not exceed this temperature, and after two hours, filtered from the separated coagulum. This was then washed with distilled water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. It weighed 0.48 gram. Before drying, this coagulum dissolved readily in two-tenths per cent. hydrochloric acid, and in dilute potash solution, and gave a violet reaction with copper sulphate and caustic potash. The filtrate from this coagulum gave a further small coagulum when heated at 70°, for some time longer. This was filtered off, and after treating it in the same way as the first coagulum, was added to it. The total amount of coagulum, preparation 39, amounted to 0.63 gram, and after drying at 110° was found to contain, ash-free, 15.23 per cent. of nitrogen.

The filtrate from 39 was then dialyzed into alcohol, and the solution thereby concentrated. On adding an equal volume of strong alcohol, the proteid was precipitated. This was filtered off, washed with absolute alcohol and ether, and dried over sulphuric acid. It then weighed 0.72 gram which shows that the proteids had been almost wholly precipitated by dialysis and coagulation.

This substance gave a nearly clear solution with distilled water, not made clearer by adding a few drops of sodium chloride solution. With caustic potash and copper sulphate, a pink color was developed which had a distinct violet tinge, and was by no means so red as that given by pure proteoses and peptones.

The aqueous solution heated to 85° gave a flocculent coagulum which apparently represented most of the substance. From

this, it would appear that true proteoses are present in extremely small amounts.

Dried at 110°, this preparation, 40, contained, ash-free, 13.60 per cent. of nitrogen. Being thrown down by strong alcohol, it could scarcely be pure, and the nitrogen determination is only of value, as indicating that the coagulum mainly consisted of proteid.

Of these preparations, 25, 27, and 32, are unquestionably mixtures of phaseolin and phaselin. Excluding these three and also 38 and 40, evidently impure, the remaining agree fairly well, as is shown by the following table:

SUMMARY OF ANALYSES OF PHASELIN FROM THE KIDNEY BEAN.

	26.	28.	29.	30.	31.	33.	
Carbon		51.57		51.59	51.98		
Hydrogen		6.92		6.71	6.82		
Nitrogen	14.57	14.48	14.81	14.84	14.53	14.85	
Sulphur, Oxygen			27.03		26.87	26.68	
		100.00		100.00	100.00		

	34.	35.	36.	37.	38.	Average.	
Carbon	51.38	51.37	51.41	52.19	51.27	51.60	
Hydrogen	6.91	7.10	7.28	7.24	7.22	7.02	
Nitrogen	14.67	14.71	14.59	14.79	14.32	14.65	
Sulphur, Oxygen		27.04	26.82	0.47, 26.25	25.78	0.51, 26.68	0.49, 26.24
	100.00	100.00	100.00	100.00	100.00	100.00	

It is probable that these analyses pretty closely represent the true composition of this proteid, the various preparations having been made under such diverse conditions as to exclude the possibility of their being mixtures of the phaselin with non-proteid substances.

Preparations 26 and 28 were precipitated by heat, 29 and 30 by acid. Preparations 31, 34 and 35 were thrown down by alcohol, extracted by water from the precipitate so produced, and separated from the solution—31 by acid, and 34 and 35 by dialysis in alcohol. Finally, 36, 37, and 38 were obtained by fractional dialysis in water.

There is some difficulty in deciding to what class of proteids phaselin should be assigned. It most nearly agrees with the

globulins, being precipitated by dialysis after nearly all the salts are removed, and thereby largely converted into an insoluble form. Complete precipitation is not accomplished, even by prolonged dialysis in distilled water, and it may be questioned whether the precipitation that occurs on dialysis in water, is not the result of transformation into "albuminate."

Nitric acid in sufficient quantity gives a precipitate which, on warming, does not dissolve in the manner characterizing proteoses. Saturation with sodium chloride, gives only a slight precipitate, but further addition of acetic acid, occasions an abundant precipitate. With copper sulphate and caustic potash a violet color is produced.

The coagulum produced by heat, dissolves in one-tenth per cent. hydrochloric acid when heated to 80°. The temperature at which coagulation commences, varies with the amount of salts present, a turbidity usually appearing between 40° and 50° in solutions which have been dialyzed until the greater part of the phaseolin had been separated. The ten per cent. sodium chloride extract of the bean-meal, became turbid at 52°–55°, flocks forming at 68°–70°. The aqueous extract of the meal, heated to 60° gave a turbidity but slightly increased by boiling. When ten per cent. of sodium chloride was added to the aqueous extract, turbidity occurred at 37° and flocks formed at 52°. The coagulation of this proteid by heat, proceeds very slowly and is completed only by very prolonged heating, for days even, at a temperature considerably higher than that at which flocks first appear.

Amount of Proteids in the Kidney Bean.

The quantities of these two proteids occurring in the kidney bean cannot be accurately determined, owing to the difficulties encountered in separating them. An approximate estimate is as follows:

1. A sample of freshly ground air-dry bean-meal yielded by combustion, 3.785 per cent. of nitrogen. Considering all the nitrogen to exist as proteids containing sixteen per cent. of this element, the proportion of proteids in the bean-meal would be $(3.785 \times 6.25 =)$ 23.65 per cent.

2. Twenty grams of bean-meal were treated repeatedly with

ten per cent. sodium chloride solution, until no more proteids could be extracted. The residue, after washing with water, alcohol, and ether, weighed, air-dry, 11.41 grams and contained 1.877 per cent. or 0.214 gram of nitrogen, equivalent to 1.338 grams of salt-insoluble proteid, which amounts to 6.69 per cent. of the meal. The salt-soluble proteids were accordingly (23.65 —6.69 = 16.96) seventeen per cent. of the meal.

3. In making preparations 4, 5, 6, and 7, pp. 638–9, the phaseolin obtained from the salt extract amounted to 14.77 per cent. This when weighed was not altogether pure or dry, but on the other hand, a part of this proteid existing in the salt extract, was not recovered, so that it may be fairly assumed that the meal contains about fifteen per cent. of salt-soluble phaseolin. This deducted from the seventeen per cent. of total salt-soluble proteids, leaves two per cent. for phaselin, reckoned water-free, other proteids being present in very minute quantity.

4. The preparations 36, 37, 39, and 40, pp. 758–60, were obtained from one and the same portion, 400 grams, of bean-meal, after phaseolin had been as completely removed as practicable. These preparations after drying over sulphuric acid, weighed respectively 6.00, 1.60, 0.63, and 0.72 grams, their total weight being 8.95 grams, equal to 2.24 per cent. of the meal. Their average nitrogen content was 14.54 per cent., very nearly that of phaselin. Making liberal allowance for impurities and incomplete drying, they represent about two per cent. of phaselin.

5. Twenty grams of bean-meal were extracted as completely as possible with two-tenths per cent. potash water. The washed and air-dry residue weighed 11.27 grams, and contained 0.91 per cent. or 0.1026 gram of nitrogen, equal to 0.611 gram of (water-free) proteid insoluble in alkali, or to 3.06 per cent. of the meal. The alkali-soluble proteid amounted therefore to (23.65 — 3.06 = 20.59) 20.6 per cent. of the meal.

6. On page 642 is recorded that the proteid insoluble in salt solution, but dissolved by two-tenths per cent. potash, 15, contained sixteen per cent. of nitrogen and accordingly had nearly the composition of phaseolin. It is, therefore, probable that the proteid undissolved by salt-solution, is phaseolin. On this assumption, the kidney bean examined, contains about 21.5

per cent. of phaseolin, and about two per cent. of phaselin.

7. The foregoing data are summarized as follows: The "white medium field bean" contains approximately:

Phaselin, salt-soluble	2	per cent.
Phaseolin, salt-soluble	15	"
Phaseolin, salt-insoluble, alkali-soluble	3.5	"
Phaseolin, insoluble in salt and in $\frac{2}{10}$ per cent. alkali	3	"
Total proteids	23.5	"

Schulze, Steiger and Maxwell have stated[1] that ten per cent. of the nitrogen of the seeds of the horse bean (*Vicia faba*) the vetch and the pea, exists in non-proteid form. Should such prove to be the case with the kidney bean, then its total proteids would be about twenty-one per cent. instead of 23.5 per cent.

Conclusion.

The kidney bean contains two globulins characterized by great solubility in very dilute saline solutions, and by yielding precipitates with acids which are soluble in sodium chloride solutions. One of these globulins, *phaseolin*, probably forms about twenty per cent. of the seed, and has the following composition, which is the average of analyses of twenty-four different preparations:

Phaseolin.

Carbon	52.58
Hydrogen	6.84
Nitrogen	16.47
Sulphur	0.56
Oxygen	23.55
	100.00

This is the proteid described by Ritthausen in 1884, to which he assigned very nearly the same composition as that above given.

The other proteid, *phaselin*, is much more soluble, remaining in solution after the phaseolin has separated. It is slowly coagulated by heat at temperatures varying with the amount of salts present and the rapidity of heating. It is precipitated by acids, on prolonged dialysis yields insoluble or albuminate modifications, and has more nearly the properties of a globulin

[1] *Versuchs Stationen*, 39, 306.

than of any other recognized class of proteids. It has an unusually low nitrogen and high oxygen content as shown by the subjoined average of the analyses of eleven different preparations.

PHASELIN.

Carbon	51.60
Hydrogen	7.02
Nitrogen	14.65
Sulphur	0.49
Oxygen	26.24
	100.00

In addition to these two globulins, the extracts were found to contain an extremely small amount of *proteose*.

MAY, 1893.

A SAFETY ATTACHMENT FOR RIDERS.

BY CHAS. E. PARKER, PH.C.

Received August 30, 1894.

SOME years since, an attachment for manipulating the weighing rider of balances was introduced by Verbeck and Peckholdt. The arrangement, devised by the writer, and here described, appears to have some advantages in simplicity, lightness, and adaptability.

It consists of a piece of sheet brass cut in the shape shown in *b*, Fig. 1, to which is soldered a bit of hair-spring from a watch, *a*; and of a light glass rod, *m*, Fig. 3, secured in a position parallel to the beam behind and slightly above it.

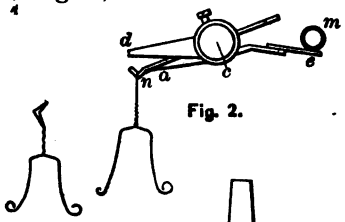


Fig. 2.

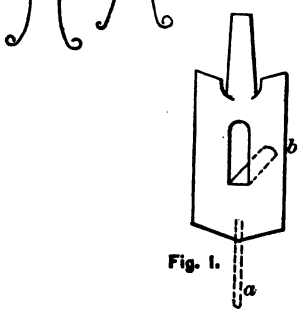


Fig. 1.

The piece of brass, *b*, is bent, as shown in Figs. 2 and 3, to form a sleeve upon the rod, *c*, together with a prong in apposition to the hook by which the rider is usually lifted, *n*, Fig. 2; and an extension, *e*, back under the rod, *m*, which thus limits the rotation of the sleeve and prong in one direction.

The operation is readily understood; the usual hook arrangement being converted into forceps

normally closed by the spring, *a*, thus securing the rider. When, by turning the rod, *c*, the rider is lowered, just before it rests upon the beam, contact between *m* and *e* checks the corresponding motion of the sleeve, thus opening the forceps; continuing

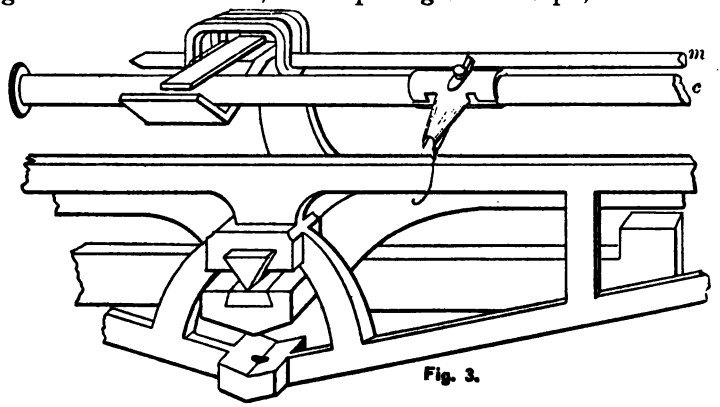


Fig. 3.

the movement, the rider is left hanging free upon the beam. Upon releasing the rod, *c*, the tension of the spring should be sufficient to close the forceps. When, however, it is often desirable to leave the rider upon the beam, by bending its loop, as shown in the side sketch, Fig. 2, this is easily effected.

Not the least advantage of this device is the readiness with which it can be extemporized.

ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE YELLOW PRECIPITATE.

By B. W. Kilgore.

Received September 15, 1894.

METHODS based upon the principle of titrating the yellow precipitate with standard alkali have been described by a number of chemists, especially for the estimation of phosphorus in iron and steel and their ores, where it is present in very small quantities. Among them may be mentioned by abstract:

E. Thilo (abstract *J. Anal. Chem.*, **1**, part 2, 219, *1887*) in the estimation of P_2O_5 in Thomas Slag, precipitates at 70° C. with molybdic solution containing one part molybdic acid, three parts ammonium nitrate, and fifteen parts nitric acid, allows to stand five minutes, filters, washes with twenty per cent.

ammonium nitrate solution, and titrates with ammonium hydroxide and back with sulphuric acid.

C. E. Manby (*J. Anal. Appl. Chem.*, **6**, 82) precipitates near boiling, washes with three per cent. each nitric acid and potassium nitrate, dissolves in fifteen per cent. ammonium hydroxide, boils off the excess of ammonia, adds two cc. of nitric acid of 1.20 sp. gr., evaporates to dryness, heats sufficiently to expel nitric acid and ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid.

J. O. Handy (*J. Anal. Appl. Chem.*, **6**, 204) precipitates at 85° C., shakes for five minutes, filters, washes five times with one per cent. nitric acid, five times with one per cent. potassium nitrate, and titrates.

M. Rothberg and W. A. Auchinvole (*J. Anal. Appl. Chem.*, **6**, 243) precipitates at 40° C., shakes for one minute, allows to stand in a warm place five more, filters, washes five times with one per cent. nitric acid, five times with three-tenths per cent. potassium nitrate, titrates with sodium hydroxide, and back with nitric acid.

Dr. Franz Hundeshagen (*Chem. News*, **60**, 168, 177, 188, 201, 215) in his analytical studies of ammonium phosphomolybdate, shows its composition under all conditions, when free of molybdic acid and other impurities, to be $12MoO_3 . PO_4 . 3NH_4$.

He washes the precipitate with five per cent. solution of ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid. He found that it required twenty-three molecules of alkali to neutralize one molecule of ammonium phosphomolybdate.

And H. Pemberton, Jr., (*J. Am. Chem Soc.*, **15**, 382) has published the description of a method on this principle, which he applied to the determination of phosphoric acid in high-grade phosphates. He uses one-tenth gram substance for analysis, precipitates at boiling with aqueous ammonium molybdate, washes with water, titrates with potassium hydroxide, free from carbonates, and back with hydrochloric acid. In his first work, he found that it required 23.2 molecules alkali to neutralize one molecule ammonium phosphomolybdate, but in his later work he has obtained twenty-three molecules.

The writer has made quite a good many determinations of phosphoric acid in materials of varying percentages by this method, with fairly good results generally but with very wide variations at times, the tendency of the method being to give high results, although the yellow precipitate was washed liberally to remove free acid. It was believed that molybdic acid was the cause of the variations, as it was known that molybdic acid would deposit from other molybdic solutions very quickly at the temperature of precipitation used in the Pemberton method. To see if the aqueous molybdate was an exception to this rule, and also to see if the official molybdate of the Association of Official Agricultural Chemists would take the place of the aqueous solution, the official molybdate was used for precipitating at boiling temperature, the method as described by Pemberton being carried out otherwise, except that two-tenths gram of substance was used.

Results obtained in this way were less subject to variations than when the aqueous molybdate was employed, though high percentages would still often be obtained. Both molybdates were then tried side by side in the water-bath at temperatures of 70°, 65°, and 60° C., (this means practically 5° lower temperature in the beaker), allowing five minutes for precipitation, which was found in all cases to be complete. The results thus obtained were favorable to the lower temperature of 60° C. in bath and to the official molybdate, there being very few variations from the gravimetric method when precipitation was made at 60° C. and by official molybdate. A great many results were obtained in testing these and other points, but most of the early ones were not kept. In the following table are brought together some of the earlier results and all of the later ones by the volumetric method, either as carried out by Pemberton or myself or both, in the order in which they were obtained, and also results by the gravimetric method on the same samples for comparison. The gravimetric results were not duplicated. Among the earlier results by the volumetric method, there are quite a number of wide variations from the gravimetric results, but the later ones by the volumetric method as carried out by myself, nearly all show close agreement with gravimetric results.

DETERMINATION OF PHOSPHORIC ACID IN VARIOUS FERTILIZERS BY THE GRAVIMETRIC METHOD AND BY THE VOLUMETRIC METHOD AS CARRIED OUT BY PEMBERTON AND AS CARRIED OUT BY KILGORE.

No.	Official.	Pemberton.	Kilgore.	No.	Official.	Pemberton.	Kilgore.
1.....	10.40		10.34[1]	35.....	10.41		10.26[4]
2.....	9.48		9.40[1]	36.....	10.43		9.46[5]
2.....			10.52[1]	37.....	12.26		9.94[5]
3.....	2.44		2.53[1]	38.....	8.83		8.84[3]
4.....	2.85		2.78[1]	39.....	8.11		8.08[4]
5.....	3.90		3.83[1]	40.....	13.36		8.87[5]
5.....			3.80[1]	41.....	10.59		10.34[3]
6.....	0.08		0.30[1]	42.....	8.83		8.56[4]
7.....	2.17	2.18		43.....	9.17		9.26[2]
8.....	2.72		2.62[1]	44.....	9.12		9.17[2]
9.....	3.76	3.76		45.....	10.20		10.33[2]
10.....	15.58		15.48[1]	46.....	13.70		13.62[2]
10.....			15.40[1]	47.....	13.92		13.92[2]
11.....	14.09		13.96[2]	48.....	15.75		15.50[2]
12.....	13.61		13.36[2]	49.....	8.14		8.40[2]
12.....			13.60[2]	50.....	8.40		8.22[2]
13.....	12.98		13.06[1]	51.....	10.73		10.80[2]
14.....	9.79	10.60	9.60[2]	52.....	9.63		9.67[2]
14.....			9.70[2]	53.....	10.50		10.48[2]
15.....	9.95	10.25	9.90[2]	54.....	10.53		10.58[2]
15.....		10.20	9.83[2]	55.....	11.13		11.10[4]
16.....	1.25		1.14[2]	56.....	8.96		8.87[4]
17.....	2.64		2.56[2]	57.....	10.75		10.72[4]
18.....	1.68		1.58[2]	58.....	10.73		10.74[4]
19.....	4.06	4.05		59.....	11.63		11.53[4]
20.....	2.07	2.10		60.....	9.59		9.64[3]
21.....	1.37	1.31[2]		61.....	13.96		14.18[3]
22.....	2.14	2.19[2]		62.....	14.43		14.33[6]
23.....	1.30		1.23[2]	63.....	14.37		14.23[6]
24.....	3.93		3.93[2]	64.....	10.67		10.65[3]
25.....	10.90	10.87		65.....	9.49		9.55[3]
26.....	11.28	11.90[2]		66.....	10.61		10.77[3]
27.....	8.89	10.55	9.00[2]	67.....	10.93		11.11[3]
28.....	10.61	10.98		68.....	11.55		11.59[6]
29.....	9.93	10.14		69.....	12.60		12.45[6]
30.....	9.72	9.98		70.....	10.16		10.45[6]
31.....	10.59	10.96		71.....	14.80		14.77[6]
32.....	9.04		9.10[3]	72.....	9.95		10.20[2]
33.....	8.72		8.72[3]	73.....	9.93		10.22[2]
34.....	10.07		10.00[4]	74.....	9.63		9.80[2]

No.	Official.	Pemberton.	Kilgore.
75.....	10.52		10.49[7]
76.....	11.00		10.98[2]
77.....	10.68		10.71[7]
78.....	13.42		13.26[7]
79.....	12.63		12.60[7]
80.....	15.06		14.89[7]
81.....	14.79		14.84[7]
82.....	14.87		14.84[7]
83.....	12.22		12.17[7]
84.....	12.75		12.72[2]
85.....	12.46		12.34[7]
86.....	11.23		11.09[7]
87.....	9.03		9.12[7]
88.....	10.49		10.40[7]
89.....	15.43		15.30[7]
90.....	16.27		15.86[7]
91.....	15.98		15.61[7]
92.....	15.71		15.71[7]
93.....	11.83		11.63[7]
94.....	10.04		9.94[7]
95.....	13.28		13.25[7]
96.....	10.55		10.42[7]
97.....	10.41		10.40[7]
98.....	9.76		9.62[7]
99.....	11.26		11.25[3]
100.....	11.49		11.37[7]
101.....	15.83		15.73[7]
102.....	15.71		15.71[7]
103.....	15.25		15.20[7]
104.....	11.64	12.15	11.63[3]
105.....	15.89	16.20	15.71[3]
106.....	15.54	16.15	15.65[7]
107.....	15.20	16.17	15.25[3]
108.....	13.96		14.18[7]
109.....	13.60		13.67[7]
110.....	15.67		15.82[7]
111.....	11.80		11.85[7]
112.....	11.74		11.75[7]
113[8]	19.93	20.35	19.85[7]
	19.83	20.15	19.95[7]
	19.91	20.15	19.90[7]
	19.85	20.10	19.80[7]
114	17.17	17.20	17.15[7]
	17.12	17.40	17.10[7]
115.....	2.42		2.47[7]

[1] Precipitated at boiling.

[2] Precipitated in bath at 70° C.

[3] Precipitated in bath at 65° C.

[4] Precipitated in bath at 65° C. with the addition of five cc. HNO_3 to fifty cc. molybdic solution (official).

[5] Same as 4 with ten cc. HNO_3.

[6] Same as 4 with three cc. HNO_3.

[7] Precipitated in bath at 60° C.

[8] C. P. $Na_2HPO_4 + 12H_2O = 19.826$ per cent. P_2O_5.

There are two main differences in the volumetric method as carried out by Pemberton and as carried out by myself. First, the temperature of precipitation in the former is at boiling; in the latter 60° in bath or 55° C. in beaker. At the former temperature molybdic acid deposits very quickly, especially if any considerable excess of the precipitant is present. If we know how much phosphoric acid our samples contain and add just enough molybdate to do the work, or are willing to add little by little of the precipitating reagent till the proper amount has been added, this objection is largely overcome, but the former we do not know and the latter is tedious and time-consuming,

especially when large numbers of analyses are being carried on at once. At 55° C., the official molybdate does not deposit, at worst, for fifteen minutes or more; precipitation is always complete in four or five minutes from the time the molybdate is added, and precipitation and filtration can be finished in almost, if not in, as short a time by this method of procedure as by the regular Pemberton method, with the advantages of less danger of molybdic acid depositing, and of being able to handle a larger number of determinations at once.

The second difference is in the two molybdic solutions. The official molybdic solution contains practically sixty grams MoO_3 to the liter, and the Pemberton solution, sixty-six grams to the liter, so there is no very great difference in their precipitating powers. In the official molybdate the proportion of free nitric acid to molybdic acid is always the same, being equivalent to nearly fifteen cc. 1.42 sp. gr. acid to fifty cc. molybdic solution; while in Pemberton's molybdate the quantity is just five cc. 1.42 sp. gr. nitric acid, no matter whether twenty-five cc. or fifty cc. of the aqueous molybdate is added. It will be readily understood that should any considerable excess of this aqueous molybdate be added (and such a thing is liable to be done), and there being only five cc. nitric acid to hold it in solution, precipitation of molybdic acid would be sure and quick. To see which of the two molybdates was most liable to deposit molybdic acid under the same conditions, the conditions being as nearly as possible those of precipitation without the phosphate, the following experiments were made: Fifty cc. official molybdate, containing three grams MoO_3 and fifteen cc. nitric acid were diluted with fifty cc. water; and to forty-five cc. of Pemberton's molybdate, containing 2.97 grams MoO_3, were added, ten cc. saturated solution of ammonium nitrate, five cc. nitric acid, and forty cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were placed in a water-bath at 60° C. The mixture of official molybdate showed no deposit for over twenty minutes, but a considerable one in one hour; the other mixture deposited seemingly the whole content of molybdic acid in less than four minutes and in fact this mixture could not be made to stand in the cold over three

or four minutes without throwing down great volumes of molybdic acid; but forty-five cc. and fifty cc. of the two molybdates are too much to precipitate the phosphoric acid from two-tenths gram substance, but not much in excess of safe quantities for most materials where four-tenths gram substance is used. With two-tenths gram substance, one-half the above quantities are about the right amounts to use. Experiments with them similar to the foregoing, were made as follows: Twenty-five cc. of official molybdate, containing one and five-tenths grams MoO_3 and seven and five-tenths cc. nitric acid were diluted with five cc. water; and to 22.5 cc. of Pemberton's molybdate, containing 1.48 grams MoO_3, were added five cc. nitric acid, ten cc. ammonium nitrate solution, and 12.5 cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were allowed to stand as before. The mixture of official molybdate deposited about as in the first experiment; the Pemberton one remained clear for ten or fifteen minutes, when it commenced to get cloudy and in twenty minutes it was milky and a heavy deposit had formed. Seventeen cc. of the official molybdate and fifteen cc. of the Pemberton one contain the same amounts of MoO_3 and when these quantities are used for precipitating equal amounts of nitric acid, five cc., are present in each case. When these amounts were diluted to fifty cc. and allowed to stand at 60° C. the deposits were the same as in the official molybdate in the two preceding experiments, which argues that the official molybdate contains about the right amount of nitric acid to prevent deposit of molybdic acid, and at the same time allow quick precipitation of phosphoric acid.

The aqueous molybdate as used in the Pemberton method works well when added in just the proper quantities, but there is not enough free nitric acid present to allow of much marginal excess. The official molybdate seems to contain a very large amount of free nitric acid. To test the effect of still larger quantities of free acid, the results in the table, as designated by the foot-notes, show that ten cc. additional nitric acid of 1.42 sp. gr. to fifty cc. molybdate hindered precipitation greatly; five cc. prevented its being complete in five minutes; while three cc. additional did not seem to interfere. The more free nitric acid

present, not to interfere with precipitation, the less liability there is of molybdic acid depositing. Just here I would add that the deposit from the official molybdic solution, at least, is not molybdic acid alone but a mixture of molybdic acid and ammonium molybdate. I found one deposit to contain 1.21 per cent. NH_3.

The volumetric method as it has given me best results is as follows: Make solution as per the official nitric and hydrochloric acid method for total phosphoric acid, redissolve two grams substance in thirty cc. strong nitric acid and five to ten cc. hydrochloric acid, measure out twenty cc. for total or forty cc. for insoluble, corresponding to two-tenths and four-tenths gram substance respectively, into a four-ounce beaker, add ammonia till precipitate just begins to form, and dilute to seventy-five cc. If much of the nitric acid was driven off in making the solution add ten to fifteen grams ammonium nitrate, otherwise this is not necessary. Digest in water-bath at 60° C., and after filtering the molybdate[1] used in the official method, precipitate in the usual way, allow to stand four or five minutes from the time the molybdate is added, filter as quickly as possible upon either a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos, or upon the Hirsch funnel, or preferably upon a porcelain disk (the disk to be covered with filter paper) with rubber rim in three-inch glass funnel, using the pump in all cases. Wash the precipitate three to five times by decantation, using fifty to seventy-five cc. water each time and agitating thoroughly, then onto the filter and till no longer acid, titrate with potassium hydroxide and back with nitric acid.

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THE QUALITY OF WATER SUPPLIES.[2]

BY WM. P. MASON.

A PAPER of some length, bearing the title "The Quality of Water Supplies," has just been presented before the American Society of Civil Engineers, at their Niagara meeting, which contains considerable matter provoking comment. The

[1] This solution is made by dissolving 100 grams molybdic acid in 417 cc. 0.96 sp. gr. ammonia, and pouring this into 1,250 cc. 1.20 sp. gr. nitric acid.

[2] Read at the Brooklyn meeting August 16, 1894.

author appears to be a believer in the power of water to spread disease; but some of the statements and quotations advanced by him would certainly go far to unsettle the public mind and cause lack of faith in the teachings of some able masters.

He says: "While water is held to be a carrier of disease germs, the writer is not aware that any investigator has ever claimed to have seen these germs in water, even under the highest powers of the microscope; and the evidence that water is such a carrier of pathogenic bacteria is obtained by inoculation from water samples, of nutrient media in test-tubes or on culture plates. The typhoid bacillus in water has never been seen with the microscope without previous cultivation of the germ in nutrient media. Nor has it ever been demonstrated, so far as the writer is aware, that the presence of bacilli in water can be proven, excepting by delicate and difficult bacteriological processes."

That single individuals of the Eberth bacillus should escape direct detection is hardly to be considered surprising, in view of the enormous volume of water in which they are suspended. However difficult the processes of modern bacteriology may be for a tyro, it is hardly just to consider them unreliable in the hands of Koch, Pasteur, or Eberth; and if any one of these men, or of many other who might be named, should state that he had secured pure cultures of a specific germ, under circumstances which excluded the possibility of extraneous contamination, we should be exceedingly liable to believe him.

Again: "It is well understood that the infective element of typhoid fever can be present in water, and the chemical test be powerless to disclose it."

True enough! but it does not complete the story. The contaminated waters were pronounced pure. It must be remembered that the polluting material, as weighed, being very largely water, the pollution appeared greater than it really was. During an investigation following a serious outbreak of typhoid fever in the Tees Valley, England, the medical officer of the Local Government Board, London, caused preparation to be made of samples of pure water, to which small quantities (fifty and twenty-five parts per million) of typhoid dejecta had been added,

and these samples were then submitted to prominent water analysts for examination. No results upon which an adverse report could be based were obtained. Fifty parts per million of the typhoid dejecta corresponded to only four parts per million of total dry residue. As a natural result of these experiments, the purely chemical methods of water examination received very severe criticism, and the advocates of the exclusively bacteriological processes were correspondingly elated, for here were known instances of fatal contamination, which the chemists had failed to diagnose. Let this, however, be said in defense: In cases as they occur in practice, a serious addition of typhoid dejecta has much that is associated with it, of a comparatively inoffensive character, but which reacts with the chemical reagents, and tells the tale of sewage contamination, although the analyst can not venture to state the exact nature of the source whence the pollution is derived.

Not long since, the writer claimed that the river water furnishing a large Eastern city was contaminated with up-stream sewage, the opinion having been based not alone upon an analysis of the water at the intake, for the river was large and the consequent dilution great, but upon the difference between that analysis and one of the water taken from above the sewage inflow. The difference was small, but it was noticeable, and there was no other sufficient explanation of its existence than the one given. Later on, typhoid fever broke out in the upper valley, and epidemics developed not only in the city in question, but in all the neighboring towns using the river water for supply. Closely related cities and towns, which received their water from other sources, were not affected. Space does not permit of giving details, showing how clearly the case stood against the river water, but it is interesting to note that typhoid germs were most carefully sought for and were not found. That they were nevertheless present, there can be but little doubt.

Chemical analysis in this instance did certainly not detect the presence of typhoid, but what it did do, was to warn the people, months before the typhoid appeared, that they were drinking diluted sewage, and that they must beware of the time when that sewage came from pathogenic sources.

The paper in question goes on to say:

"The popular impression that the Koch or Finkler and Prior comma bacillus is the cause of cholera is fallacious, or, at least, not proven. The same remark applies to the typhoid bacillus of Eberth. The proof is still wanting that this will cause typhoid." This last is a quotation from Sternberg's Manual of Bacteriology, but it is very misleading because it is incomplete.

What Sternberg really says is this: "Recent researches support the view that the bacillus described by Eberth, in 1880, bears an etiological relation to typhoid fever; and pathologists are disposed to accept this bacillus as the veritable germ of typhoid fever, notwithstanding the fact that the final proof that such is the case is still wanting. This final proof would consist in the production of man, or in one of the lower animals, of the specific morbid phenomena which characterize the disease in question, by the introduction of pure cultures of the bacillus into the body of a hearty individual. Evidently it is impracticable to make the test upon man, and thus far we have no satisfactory evidence that any one of the lower animals is subject to the disease, as it manifests itself in man." Now that is a very different statement, and conveys a meaning greatly unlike the one suggested by the partial quotation referred to.

The paper says: Absolutely healthy persons have been known to reject the Eberth bacillus in their excrement, showing such, probably, to be in the intestines at all times." This is an error. To use the words of Sternberg, from whom the paper so often quotes: "No competent bacteriologist, so far as I know, has claimed to find the Eberth bacillus in the feces of healthy individuals."

As to the doubt thrown upon the correctness of the view that Koch's comma bacillus is the cause of cholera, the work of Sternberg will hardly endorse it. In this connection Sternberg says: "The etiological relation of this spirillum to Asiatic cholera is now generally admitted by bacteriologists," and also, "the most satisfactory evidence that this spirillum is able to produce cholera in man, is afforded by an accidental infection which occurred in Berlin in the case of a young man who was one of the attendants at the Imperial Board of Health when

cholera cultures were being made for the instruction of students."

As to the statement in the paper that "fatal cases of typhoid have been attended with none of the Eberth bacillus in the feces, or in the intestines, the seat of the disease," it is to be noted that Gaffky's investigations show it to be by no means a serious objection. He considers the technical difficulties surrounding a hunt for the bacillus in some few instances so considerable as to readily account for a small percentage of negative results, and he cites instances where he found the "germ" after an amount of patient search extending far beyond the point where the average observer would have ceased work and placed a negative report upon record.

Finally, the paper has much to say upon the imperfections of modern filters and the danger of using water therefrom. It goes without saying that pure water is better than purified water, but then the former is often unattainable, and we have to do with the latter or go without.

The paper lays especial stress upon the fact that even when the filtration is so successfully accomplished as to leave in the filtrate only one or two bacteria per cubic centimeter, yet "a person may imbibe from 250 to 500 bacteria in drinking a single glass of water, some of which may be pathogenic and produce typhoid fever, or some less dangerous disease." Such a degree of excellence in filtration as the obtaining of a filtrate with only one or two bacteria per cubic centimeter is indeed rarely attained, yet the public have a right to look with confidence upon a plant which does not pretend to accomplish half that amount of purification.

Consider for a moment what the Altona filters did for that city during the Hamburg cholera epidemic of 1892. The Altona water was taken from the Elbe river at a point below the outfalls of sewers carrying the cholera-infected sewage of 800,000 people. Yet Altona had but very little cholera (except imported cases), while Hamburg was scourged by it. The cities are practically one, a stranger being unable to tell the dividing line.

Take the numbers showing the efficiency of the Altona filters during one month of 1892:

The bacteria in the raw Elbe water per cubic centimeter varied from 9,370 to 44,140, with an average of 28,667. The average number in the filtered water was ninety. This meant a removal of 99.69 per cent. of germs of all kinds, 0.31 per cent. still remaining. The filtrate was by no means sterilized, but the city was protected from a cholera epidemic under circumstances trying in the extreme. As to the efficiency of sand filtration for water purification, the following figures are given for results found at the Lawrence experiment station, the filters having been operated with water containing known quantities of bacteria:

Rate in gallons per acre daily, 1,500,000; kind of bacteria added, B. typhi. abdom.; per cent. removed, 99.93; rate in gallons per acre daily, 3,000,000; kind of bacteria added, B. prodigiosus; per cent. removed, 99.95.

This reduction of the number of germs in a given volume of water is possibly equivalent to a dilution of the unfiltered water with a very large volume of a pure supply; and in this connection the writer of the paper says: "Dilution may reduce the chances of any single individual imbibing a fatal germ, but the germ itself will be just as dangerous when it is imbibed."

This is, doubtless, true if the individual be especially susceptible, for it has been experimentally shown that a single germ may produce fatal results when injected into an animal very prone to the special disease, but it has been also shown that when the animal is not very susceptible, the "dose" of bacteria has to be enormously increased to produce any result. We incline to believe that some similar reason may account for the apparent immunity of that fraction of a community, which has been equally exposed but which escapes contagion.

What the paper says regarding the unsatisfactory results observed where household filters are in use, is, unfortunately, very true, but the fault is more commonly with the attendant than with the filter. The common belief is that a filter, once established, is good for all time, and I could tell tales of what I have seen, in otherwise well-organized establishments, that would stagger belief. I do not approve of general household filtration, as I believe purification can be better and more cheaply done on

the large scale by the municipal authorities, but I can not think that the Pasteur filter should be swept aside like the worthless contrivance the paper calls it. My experience is that, with proper care, it is efficient. Extended tests were made with it for the Connecticut Board of Health in 1892, which show that it may be depended upon, if the procelain cylinder be cleaned and sterilized once a week.

Freundenreich has obtained similar results, and has also shown that the length of time during which the filter is efficient depends upon the temperature.

RENSSELAER POLYTECHNIC INSTITUTE,
August, 1894.

THE PROTEIDS OF COTTONSEED.[1]

BY THOMAS B. OSBORNE AND CLARK G. VOORHEES.

THE only reference to the proteids of cottonseed which we can find was made by Ritthausen in 1881 (*J. prakt. Chem.*, **23**, 485), who stated that he had been unable to obtain crystals of proteid matter from this seed and also that he would soon publish his complete investigations of the proteid bodies of this as well as of several other seeds which he named. Papers on the proteids of the other seeds mentioned by him were subsequently published, but we have not found anything relating to those of cottonseed. Since so long a time has elapsed, we feel warranted in assuming that Ritthausen has abandoned his intention of reporting the results of his investigation. The importance which cottonseed-meal has assumed as a cattle-food of late years, makes it desirable to understand its chemical composition, especially as regards the nitrogen compounds which it contains so abundantly. Our results are not as satisfactory as we hoped for when we undertook this work but we have decided to publish them as they stand and shall endeavor to make them more complete in the future. The difficulties encountered are due to the presence of substances which render filtration of the extracts extremely slow and to the large amount of coloring matters taken up from the seed together with the proteids, which could be separated only with difficulty and large loss of substance. The material used in our investigation consisted partly of seed

[1] First printed in the Report for 1893 of the Connecticut Agricultural Experiment Station.

from which the cotton had been removed, but which otherwise was in the condition in which it was harvested. We separated the kernels from these seeds by chopping them in a wooden bowl and sifting out the larger fragments of husk. We thus succeeded in obtaining meal nearly free from hulls. This meal was bruised in a mortar and freed from most of the oil by extraction with benzine and from benzine by drying in the air at the temperature of the room. Samples of commercial cottonseed-meal from which the oil had been expressed by the usual process were also used and gave the same result when extracted, and therefore in the following account of our experiments, no special mention is made of the origin of the meal employed.

a. Extraction with Water.—100 grams of cottonseed-meal were extracted with three liters of distilled water and the filtered extract saturated with ammonium sulphate. The small precipitate so produced was filtered off, dissolved in water, the solution filtered clear and placed in a dialyzer. After remaining a week in running water, no precipitation occurred, showing the absence of any notable quantity of globulin soluble in the dilute saline solution produced by the salts of the seed with the water used in the extraction. The dialyzed solution gave no immediate coagulum on boiling, proving the absence of albumens. The solution was then evaporated over a lamp and, after boiling some time, a light, bulky coagulum gradually separated. When the solution became quite concentrated, the coagulum was filtered off, washed with water, alcohol, and ether, dried over sulphuric acid and found to weigh 0.25 gram. The filtrate from this coagulum was evaporated to small volume on a water-bath and precipitated by pouring into absolute alcohol. The precipitated proteid was then washed with absolute alcohol and ether and weighed, when dry, 0.40 gram. Accordingly, 0.65 per cent. of the oil-free meal, consisted of water-soluble proteose-like matter. The amount of this substance was so small, and the difficulty of preparing it in a state of purity so considerable, that it was not further examined. Other experiments, both with water and saline solution, fully confirmed the results here described and left no doubt that the amount of water-soluble proteid is very small.

b. Extraction with Sodium Chloride Solution.—When treated with ten to twenty per cent. sodium chloride solution, the cottonseed-meal yields a slightly acid extract of a yellowish-pink color which is viscid, and difficult to filter. When heated slowly, this extract becomes turbid at 44°, flocks, in small amount, separating at 64°. Filtered after heating to 70°, the solution becomes turbid when heated again to 70° and flocks in larger amount separate at 93°.

Saturation with sodium chloride gives a slight precipitate. Dilution of the extract with water yields an abundant precipitate which is redissolved on warming and again separates in the form of spheroids when cooled.

Fifty grams of oil-free meal were extracted with ten per cent. sodium chloride solution, and the meal washed with the same solution as long as any proteid could be extracted. The extract and washings were saturated with ammonium sulphate, the precipitate produced filtered off, dissolved in dilute sodium chloride brine, filtered, and dialyzed four days. The solution was then removed from the dialyzer and the precipitated globulin filtered off, washed with water, alcohol, and ether, and dried over sulphuric acid. There was thus obtained seven grams or fourteen per cent. of light yellowish proteid which, when dried at 110°, had the composition given below, preparation 1.

A second preparation was made by treating 100 grams of meal with three liters of twenty per cent. sodium chloride solution for forty-eight hours and, after filtering, saturating the extract with ammonium sulphate. The meal-residue was again treated with twenty per cent. sodium chloride brine and after filtering the extract, it was saturated with ammonium sulphate and added to the first.

The ammonium sulphate precipitate was filtered off and dissolved in ten per cent. sodium chloride solution, yielding a deep brown liquid. This was filtered clear and dialyzed till free from chlorides when the precipitate was filtered off and treated in the usual way. There resulted 15.83 grams of globulin of a slightly yellowish color which had the composition stated below, preparation 2.

A third preparation was obtained by extracting 100 grams of

meal with water and then treating the residue with twenty per cent. sodium chloride solution.

The salt-extract was filtered, saturated with ammonium sulphate and otherwise treated in the manner already described in making preparations 1 and 2. Only 8.39 grams of globulin were recovered, indicating a conversion into the insoluble modification through contact with water.

The composition of this preparation 3, is shown by the following figures.

COTTONSEED GLOBULIN.

	1				2				3	
	I.	II.	Av.	Ash-free.	I.	II.	Av.	Ash-free.		Ash-free.
Carbon	51.85		51.85	51.91	51.75		51.75	51.86	51.66	51.77
Hydrogen	6.78		6.78	6.79	6.87		6.87	6.88	6.73	6.74
Nitrogen	18.02	18.12	18.07	18.09	17.90	18.15	18.03	18.07	17.93	17.97
Sulphur	0.68		0.68	0.68	0.67		0.67	0.67	0.71	0.71
Oxygen				22.53				22.52		22.81
Ash	0.11		0.11		0.21		0.21		0.22	
				100.00				100.00		100.00

The properties and composition of this substance are so similar to those of the vegetable vitellin found in the seeds of flax, hemp, wheat, and other seeds, it seemed probable that the three preparations just described were not entirely pure and that if freed from all foreign matters they would agree more closely with the globulin of the seeds just named. Three preparations were accordingly made, substantially in the manner already described and, after drying over sulphuric acid, they were redissolved in ten per cent. sodium chloride brine and the resulting clear solutions were dialyzed. The globulin thus reprecipitated, was filtered off, thoroughly washed with water, alcohol, and ether and when dried at 110° analyzed with the following results:

COTTONSEED GLOBULIN. EDESTIN.

	4		5		6			
		Ash-free.		Ash-free.	I.	II.	Av.	Ash-free.
Carbon	51.59	51.75	51.56	51.93	51.68	51.58	51.63	52.05
Hydrogen	6.68	6.70	6.92	6.97	7.11	6.92	6.97	7.02
Nitrogen	18.72	18.78	18.40	18.52	18.66	18.40	18.53	18.68
Sulphur	0.75	0.75	0.50	0.51	0.66		0.66	0.66
Oxygen		22.02		22.07				21.59
Ash	0.33		0.74		0.82		0.82	
		100.00		100.00				100.00

We next attempted to detect the presence of other globulins in the sodium chloride extract. One kilogram of cottonseed-meal was extracted with ten per cent. sodium chloride solution and as the extract after straining through cloth was quite concentrated and could not be filtered, it was shaken with ether so as to remove oil and other substances soluble in that liquid. On standing, a part of the aqueous solution separated, leaving a supernatant layer consisting of an emulsion which long standing failed to resolve. Addition of alcohol, instead of breaking up the emulsion, transformed it into a jelly-like mass of considerable solidity. The unemulsified part of the extract, after standing some time, was decanted and dialyzed free from chlorides. The dialyzed solution was allowed to stand until the globulin had deposited when the supernatant liquid was decanted. The separated globulin was treated with ten per cent. sodium chloride brine and the solution filtered very nearly clear. This solution was then dialyzed for eighteen hours, during which time a large precipitate formed which was filtered off, washed with water, alcohol, and ether, and, when dried over sulphuric acid, weighed 23.63 grams, preparation 7. The filtrate was found to be practically free from proteids. The solution decanted from the first precipitation of the globulin contained a large amount of very finely divided substance that would not settle. A little sodium chloride was therefore added which dissolved the suspended globulin. The solution was next saturated with ammonium sulphate and the large precipitate filtered off, dissolved in water, the solution filtered perfectly clear, and dialyzed for several days. It was then removed from the dialyzer and allowed to stand until the suspended globulin had mostly settled out. The milky solution was then decanted from the sediment and the latter washed with water, alcohol, and ether. After drying over sulphuric acid it weighed 8.58 grams. Preparation 8. The solution decanted from 8, after repeated filtration was obtained clear and was again dialyzed. After several days a very small precipitate formed which, when subjected to the usual treatment, weighed but 0.82 gram. This was much colored and evidently impure. The solution filtered from this precipitate was saturated with ammonium sulphate and yielded

only a very small precipitate which appeared to consist mostly of proteose. The emulsion obtained by shaking the original extract with ether, after standing some days, gave no evidence of re-solution. The jelly-like mass was therefore broken up and thrown on a filter. A clear quick-running filtrate was obtained which was dialyzed for five days and deposited a globulin, that, after the usual treatment, weighed 8.43 grams. Preparation 9. All these preparations were analyzed with the following results:

	Cottonseed Globulin. Edestin.							
	7				8		9	
	I.	II.	Av.	Ash-free.		Ash-free.		Ash-free.
Carbon	51.59	51.45	51.52	51.75	51.38	51.44	51.10	51.33
Hydrogen	7.04	6.70	6.87	6.90	6.70	6.70	6.88	6.91
Nitrogen	18.76	18.71	18.74	18.82	18.49	18.51	18.47	18.55
Sulphur	0.61		0.61	0.61		23.05	0.60	0.60
Oxygen				21.92				22.61
Ash	0.46		0.46		0.12		0.46	
				100.00		100.00		100.00

The above analyses show that the first three preparations were not quite pure and the extract, last made, affords satisfactory evidence that no other salt-soluble globulin exists in the cotton-seed in noteworthy amount. In the following table, the analyses of the purer preparations may be compared together.

Summary of Analyses of Cottonseed Globulin. Edestin.

	4	5	6	7	8	9	Average.
Carbon	51.75	51.93	52.05	51.75	51.44	51.33	51.71
Hydrogen	6.70	6.97	7.02	6.90	6.70	6.91	6.86
Nitrogen	18.78	18.52	18.68	18.82	18.51	18.55	18.64
Sulphur	0.75	0.50	0.66	0.61	23.05	0.60	0.62
Oxygen	22.02	22.08	21.59	21.92		22.61	22.17
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The table subjoined shows that this substance agrees in composition with the vitellin which exists in the seeds of wheat, maize, hemp, castor-bean, squash, and flax. As the properties of the preparations obtained from all these sources are substantially alike, there can be little doubt that one and the same proteid exists in them all. For this body we adopt the name *Edestin*, from the Greek εδεστος, signifying edible, in view of its occurrence in so many important food-stuffs.

COMPOSITION OF EDESTIN FROM VARIOUS SEEDS.

	Wheat kernel.	Maize kernel.	Hemp-seed.	Castor-bean.	Squash seed.	Flax-seed.	Cotton-seed.
Carbon.....	51.03	51.71	51.28	51.31	51.66	51.48	51.71
Hydrogen..	6.85	6.85	6.84	6.97	6.89	6.94	6.86
Nitrogen...	18.39	18.12	18.84	18.75	18.51	18.60	18.64
Sulphur ...	0.69	0.86	0.87	0.76	0.88	0.81	0.62
Oxygen	23.04	22.46	22.17	22.21	22.06	22.17	22.17
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The considerable differences in carbon and nitrogen in the above analyses amounting, in the extreme cases, to 0.7 per cent. are, in general, not greater than the discrepancies between analyses of preparations from the same seed. In the seeds of wheat and maize, other water and salt-soluble proteids occur in considerable quantities and it is probable that the crystallized preparations obtained from hemp, castor-bean, squash, and flax more truly represent the composition of edestin than the amorphous or spheroidal substance yielded by the cereal seeds.

The slight differences in the deportment of solutions of these preparations of edestin may be reasonably attributed to admixtures of traces of other proteids.[1]

c. Extraction with Potash Water.—After extraction with water and sodium chloride solution a considerable amount of proteid was always found in the residual-meal which could be partly removed by two-tenths per cent. potash solution. All attempts to obtain the proteid thus extracted in a pure state, have hitherto entirely failed. Much coloring matter passes into the alkaline solutions, and when the proteid is precipitated, goes down with it and can not be removed by any process we have hitherto applied.

When freshly prepared, the alkaline extracts, as well as the meal moistened with the alkali, are of a bright reddish-yellow color, but on exposure to the air they rapidly darken and finally become greenish-black. So much gummy matter is also extracted by alkaline solutions that it is almost impossible to filter them clear. As a result no preparations were obtained, the analysis of which could shed any light on the composition of the proteid which they represented. The residue of meal after treatment with potash still contains a notable quantity of nitrogen.

[1] See paper on Crystallized Vegetable Proteids, by T. B. Osborne, *Am. Chem. J.*, 1 688.

d. Amounts of the Different Forms of Proteids in Cottonseed.— As already shown, the proteid matter of cottonseed soluble in water, consists almost wholly of proteose. Making full allowance for incomplete extraction and loss, this does not exceed 0.75 per cent. of the oil-free meal. The highest yield of globulin recovered in the preceding extractions was 15.83 per cent. of the oil-free meal, and contained 42.3 per cent. of the total nitrogen. After repeated extraction with potash water, the residue contained, in the case where extraction was most complete, 11.4 per cent. of the total nitrogen, showing that 88.6 per cent. of the total nitrogen had been dissolved. The difference between the percentage of nitrogen removed by sodium chloride solutions and that extracted by weak potash, represents the proteid dissolved by potash water which is not soluble in saline solutions, and which corresponds to 46.3 per cent. of the total nitrogen, assuming all this nitrogen to be present in proteid form.

These data may be tabulated as follows:

	Per cent. of Air-dry and oil-free meal.	Total nitrogen.
Proteose	0.75	2.0
Salt-soluble proteid. Edestin	15.83	42.3
Alkali-soluble and salt-insoluble proteid		44.3
Proteid insoluble both in salt and alkali		11.4
		100.0

ON THE ANALYSIS OF AMERICAN REFINED COPPER.[1]

By Harry F. Keller.

IT is generally conceded that the presence even of minute quantities of other elements in metallic copper has a marked influence upon its physical properties, and especially upon its electric conductivity.

The copper produced in the Lake Superior region is relatively free from injurious admixtures, and is, therefore, generally preferred when a high conductivity is desired. "Lake" copper is always quoted a trifle higher than the metal from other localities.

Of late years the production of copper from impure sulphide ores has grown enormously, and, at the same time, the quality of the product has steadily improved. It has, indeed, become

[1] First printed in the Journal of the Franklin Institute, July, 1894.

possible through the introduction of the Manhés converter and the electrolytic process of refining, to obtain from matte a metal nearly, if not quite, as pure as the native copper of Lake Superior. Unfortunately, it appears that the very slight traces of the impurities retained in it affect the conductivity to a greater extent than is the case in the best lake copper. Silver and iron are the chief impurities of the latter, while electrolytic copper not infrequently contains small quantities of bismuth, antimony, arsenic, selenium, and tellurium.

That the exact manner in which these elements affect the physical properties of copper is not better understood, is, undoubtedly, owing to the lack of rapid, and at the same time accurate, methods of ascertaining their relative amounts. It is astonishing to note that the works on quantitative analysis, published in the English language, entirely neglect copper analysis. To my knowledge the important contributions to this subject by Hampe, Fresenius and other German chemists have not been translated.

For several years past I have given considerable attention to this subject. My analyses include the metal from the Lake mines, as well as copper obtained from Western mattes.

To the former, I found Hampe's original method[1] of analysis well adapted. This consists essentially in precipitating, by electrolysis, the greater part of the copper, and separating the metallic impurities in the usual manner from the remaining solution. The non-metallic elements such as oxygen and sulphur, are determined in separate portions of the sample.

For obvious reasons it is not desirable to employ this method in analyzing electrolytically refined copper. Accurate results can be obtained by following the plan proposed by Fresenius,[2] but the separation of large quantities of copper by means of hydrogen sulphide, and the difficulty of accurately weighing bulky solutions, render this method very objectionable. A far more convenient process is the one recently published by Professor Hampe.[3] It is also more rapid than either of the two methods mentioned, and, with some modifications, it is especially

[1] *Ztschr. f. Berg. Hütten u. Salinenwesen*, 21, 218, and 22, 93.
[2] *Ztschr. anal. chem.*, 21, 229.
[3] *Chem. Ztg.*, *1893*, 92, 1691.

well adapted for the analysis of most of the American refined coppers.

The process depends upon the removal of most of the copper as cuprous sulphocyanate.

The manner in which I practice it is briefly as follows:

Twenty-five grams of material are placed in a tall, lipless beaker and treated with a mixture of 200 cc. of water, forty-five to forty-six cc. of nitric acid (sp. gr. 1.21), and twenty-five cc. of concentrated sulphuric acid (in case that much antimony or bismuth is present, as much as 100 cc. of sulphuric acid may be taken). The beaker is covered and heat applied until nitrous fumes are no longer given off and the solution then diluted with 200 cc. of water to prevent the separation of copper sulphate. A rapid current of sulphur dioxide is now conducted into the liquid, the temperature of which is maintained at about 40° C. When the nitric acid is destroyed and the red fumes have disappeared, the liquid becomes turbid, owing to the precipitation of silver, selenium, and tellurium. To insure the complete separation of the silver, a drop or two of hydrochloric acid may be added. After standing for twenty-four hours in a warm place, the solution is poured through a small filter into a graduated flask of two liters capacity. It may contain bismuth, antimony, arsenic, iron, nickel, and cobalt.

The sediment retained by the filter is composed of gold, silver, silver chloride, selenium, tellurium, possibly also lead sulphate, and traces of bismuth and antimony.

To determine the elements in the filtrate, the greater part of the copper must first be removed. To this end a measured amount of standard potassium sulphocyanate solution (one cc.= 0.05 Cu) is gradually added, whilst a current of sulphur dioxide is passed into the liquid. An excess of the sulphocyanate should carefully be avoided; it is preferable to leave some of the copper in the solution which should now emit a perceptible odor of sulphur dioxide. The delivery-tube is withdrawn and rinsed off into the flask, the contents of which are then made up to the mark. To effect a thorough mixing it is well to pour the contents into a dry beaker, and to retransfer them several times from one vessel to the other. The precipitate is allowed to set-

tle and an aliquot portion, say 1,800 cc. of the solution, filtered off. The separation and estimation of the different metals is effected according to the usual analytical methods. It is hardly necessary to state that the sulphur dioxide must be expelled before hydrogen sulphide is passed into the liquid.

In calculating the amounts of the metals contained in the entire liquid, we must allow for the volume occupied by the precipitate. According to Hampe, the specific gravity of the sulphocyanate is nearly three, and since twenty-five grams of copper would give about forty-eight grams of this salt, the volume of the latter would be sixteen cc. The actual volume of the solution, therefore, is $2{,}000 - 16 = 1{,}984$ cc. Suppose *e. g.*, we had filtered off 1,800 cc., and found in it 0.020 gram of arsenic, then

$$\frac{1984 \times 0.02}{1800}$$

would be the amount of arsenic in the sample taken.

There yet remains to describe the analysis of the insoluble portion from which the main solution was filtered. It may contain, as I have already said, gold, silver (both in the metallic state and as chloride), selenium, tellurium, lead sulphate, and traces of bismuth and antimony, occasionally also copper.

It is best to detach, as completely as possible, the dry mixture from the filter, and to destroy the latter with fuming nitric acid in a small porcelain casserole. The detached portion is then added, and treated with the nitric acid till completely oxidized. After evaporation on the water-bath of the free nitric acid, the residue is digested with dilute hydrochloric acid, which leaves the silver in the form of chloride. This is filtered off, purified, and determined in the usual way. From the filtrate, selenium and tellurium may be thrown down by means of hydroxylamine hydrochloride. In the cold this reagent seems to have little effect, but upon warming, a reddish turbidity is observed which gradually collects in the form of dark flakes. These represent all the selenium and tellurium; they are collected on a tared filter and dried at 105°–110° C. to constant weight.

I have not been able to effect a clean separation of the two elements. Approximate estimations were made by fusing the

mixture in a current of hydrogen with potassium cyanide; the aqueous solution of the fused mass was then exposed to the air, which causes most of the tellurium to separate.

Gold, lead, and the traces of antimony and bismuth are determined by the ordinary methods.

NEW BOOKS.

SELECT METHODS IN CHEMICAL ANALYSIS, CHIEFLY INORGANIC, BY WILLIAM CROOKES, F. R. S., ETC., ETC.; EDITOR OF "THE CHEMICAL NEWS." Third edition, rewritten and enlarged; illustrated with sixty-seven wood cuts. London, and New York; Longmans. 1894. Price $8.

This book is without padding and is but a bare, yet voluminous, statement of analytical fact. It is sufficiently explanatory to meet the wants of the average worker. It is minute in important details. It gives concise and clear, yet full, directions for separation and determination of all known elements, and has something to say of the hypothetical ones. And while but little is stated concerning those processes well understood by analysts, there is set forth about all which concerns the newer and verified ones. The book contains a skillful digest of the best of analytical literature down to the middle of the present year.

After the preface, come thirteen pages of index to captions. The next forty-two pages are given to potassium, sodium, lithium, cesium, rubidium, and ammonium, stating several methods for determination of each of them when found in various combinations. Chapter II relates to barium, strontium, calcium, and magnesium. The third chapter gives sixty-eight pages of the masterly digest of the literature pertaining to cerium, lanthanum, didymium, samarium, thorium, glucinum, the yttrium metals, titanium and zirconium. In all, there are 697 octavo pages of analytical methods and processes, followed by a copious index to subjects and to authors' names. There is little risk in stating that the advanced worker will here find, at least, something he did not before know regarding his own immediate field. The volume is invaluable.

The author has something to say to him who is constrained to use chemistry as the carpenter does his rule, and the least

possible of it; but he has a great deal more to say to him who desires a higher and better knowledge. He forgets how profoundly we are taught that matter is divided into common and rare elements. He keeps before him the necessity of giving to all forms of matter the same kind and quantity of study. Realizing that most rare elements are rare in quantity only, and that their distribution is indeed wide, he has given us the only English-written book to which workers in chemical and metallurgical technology can, under all circumstances, refer: workers whose necessities require that they shall be as familiar with many rare elements as they are with iron and with oxygen.

The great majority of American chemists regard Prof. Crookes as an honest and earnest and most consummate analyst. The small remainder, which does not so consider him, consists of those who do not know his work. One consults him with the comfortable feeling that his statements already are verified, that they have come out of his laboratory note-book, and that if possibly he should not give the solution of the problem in hand, he quite surely will teach enough to make the remainder apparent.

In the preface to this third edition, the author states that he desires the volume to be regarded chiefly as a collection of novel or little-known processes which have been found to be successful. He has not set himself the task of printing again that which may be found abundantly in special literature; except, that he has felt impelled to give to the world a series of electrical separations and processes. After a critical examination of the volume, the reader will emerge with a consciousness that the author kept to his assigned task and that his work was well done.

WILLIAM GLENN.

BALTIMORE CHROME WORKS,
October, 1894.

A CHEMICAL AND METALLURGICAL HANDBOOK. By J. H. CREMER, M.E., and G. A. BICKNELL, B.Sc. pp. 280. Cleveland, Ohio: J. B. Savage. Price, $2.50.

This book contains 280 pages of information chiefly in notes and tables, which is of especial importance to iron chemists and metallurgists, and which any practical chemist or metallurgist

needs in a form convenient for reference. The extended and successful experience of the authors in the chemistry and metallurgy of iron is an assurance of reliability.

In the tables of logarithms and reciprocals, factors and logarithms for the calculation of analytical results, the specific gravity of solutions, and in the table giving the molecular weights, specific gravity, melting-points, boiling-points, and solubility of the principal inorganic compounds, chemists will find much useful information. The tables for the analysis of iron ores facilitate the calculation of phosphorus, silicon, and sulphur. Moisture tables are inserted for the calculation of the percentage of iron, silicon, manganese, and other constituents in the ore in its natural condition from analysis of the dried ore. As an example of the careful effort expended in the preparation of this book, the phosphorus table gives the percentage of phosphorus in pig-iron, from the percentage of phosphorus and the percentage of iron in the ore, for a difference of 0.001 per cent. from 0.001 per cent. up to 0.100 per cent. Other data include a table of fractional parts of numbers in tenths from one to eighteen for the calculation of phosphorus and silicon in an ore burden, and a table which gives the cost per unit of iron from the price and analysis of the ore in differences of one-half per cent., or iron from forty to seventy per cent.

For the convenience of metallurgists and prospectors in the field, a brief outline of the principal geological formations is included. The principal minerals are given with their chemical composition and physical properties. Other tables contain the amounts of limestone required to produce slags of different composition, the quantity of slag produced, and numerous other data that every blast-furnace manager must have constantly at hand. Brief notes on the properties and mutual relations of carbon, silicon, sulphur, phosphorus, and manganese in blast-furnace practice, contain much useful information. The book is well printed and neatly bound. CHARLES F. MABERY.

NOTES.

Changes in Official Methods of Soil and Ash Analysis.—The following are the principal changes in methods of soil and ash analysis adopted at the last meeting of the Association of Official Agricultural Chemists:

1. A sieve with circular openings one-half mm. in diameter is to be used in preparation of the fine earth for analysis.

2. Moisture is to be determined in the air-dried, prepared sample by drying a weighed portion to constant weight in a water-oven, the water of which is kept briskly boiling.

3. The digestion is to be done in a flask provided with a return condensing tube and heated for ten hours continuously in boiling water; ten grams of soil and 100 cc. of HCl of sp. gr. 1,115 are to be used, and the solution is to be made up to 500 cc. and aliquots taken for analysis, except where the insoluble residue exceeds ninety per cent., in which case twenty grams are to be used with 100 cc. of acid. Larger quantities of soil may be used if the proportion of acid and amount of dilution be preserved.

4. The silica soluble in Na_2CO_3 solution is to be separated before the ignition of the "insoluble residue" in both ash and soil analysis.

The methods of analysis are essentially the same as those provisionally adopted for the past two years, but as they have been rewritten and revised, it is necessary to refer to the forthcoming proceedings for the details. The proceedings are now in the hands of the printer and will soon be ready for distribution.

The recommendation of the reporter, that the question of the determination of available P_2O_5 and K_2O in soils, particularly by the action of dilute organic acids, be made one of the subjects for investigation next year, was also adopted.

ALFRED M. PETER,
Reporter on Soil and Ash, A. O. A. C.

LEXINGTON, Ky., Oct. 3, 1894.

ERRATUM.—Page 650, October 1894, fifteenth line, for *Amelia* read *Amherst.*

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THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDATE-MAGNESIA METHOD.

BY B. W. KILGORE.

Received September 15, 1894.

FOR the investigation of the official molybdate method as used by the American Association of Official Agricultural Chemists for 1894, three samples were sent to various agricultural and commercial chemists with instructions for analysis.

No. 1 was a mixture of cottonseed-meal and castor pomace, containing about two and one-half per cent. P_2O_5.

No. 2 was an acid phosphate with about seventeen per cent. P_2O_5.

No. 3 was a phosphate solution containing ten grams C. P. disodium hydrogen phosphate ($Na_2HPO_4 + 12H_2O$) to the liter, the theoretical percentage of P_2O_5 in this salt being 9.826.

The discussion, which will be made here, of this work will be confined to the results obtained on solution No. 3, as it was the only sample whose content of P_2O_5 was definitely known. Twenty-eight chemists reported thirty-four determinations on No. 3, the highest of which was 20.67 per cent., and the lowest 19.74 per cent., the latter being 0.086 of one per cent. below the theory, and the former 0.844 per cent. above. The average of all results was 20.09 per cent., or 0.264 of one per cent. above the theory; the variation between highest and lowest results was 0.93 of one per cent.; the variation below the theory was 0.086 and above the theory 0.844 of one per cent. Eighteen per cent. of the determinations were within 0.05 of one per cent. of the theory, thirty-six per cent. within one-tenth, and forty-four per

cent. within two-tenths. In the work on this sample a few analysts have gotten results reasonably close to the theory, a great many have varied widely from it, and nearly all have gotten high results, which brings me to the point to which I desire to draw especial attention, and that is the tendency of the molybdate-magnesia method to give high results, even when the greatest care is exercised as is reasonable to suppose was the case in this test work. I might add here that nearly all the chemists taking part in this work had had some years experience with the method, and those who had not, worked under good supervision.

The tendency of the method then, it seems, is for high results, and it is in order to ask where the trouble lies.

The phosphate solution sent out was precipitated directly with magnesia mixture by four chemists, when they obtained (1) 19.92, (2) 19.93 and 19.94, (3) 19.91 and 19.85, and (4) 20.03 and 20.05 per cent. P_2O_5, against (1) 19.93 and 19.87, (2) 19.93 and 19.91, and (3) 19.93 and 20.06 by precipitating with molybdic solution first.

The results here by both methods of procedure, while slightly high, most of them, are practically the same whether precipitation was made direct with magnesia mixture, or previously with molybdic solution. This argues that the trouble is not in the molybdate precipitate or precipitation. The magnesium ammonium phosphate precipitate obtained from this sample in the usual way was, after washing, dissolved by one chemist in hydrochloric acid and reprecipitated with ammonia, when he obtained 19.80 and 19.81 per cent. P_2O_5, while another added one gram citric acid to the alkaline solution in which the "white precipitate" is formed and obtained 19.83 and 19.83 per cent. P_2O_5 against 20.06 and 19.93 by the regular method.

The results by the last two methods of procedure are, while few, close to the theory and indicate that in the regular molybdate-magnesia method that either some of the magnesium of the magnesia mixture is thrown down as hydroxide and contaminates the precipitate, or else the magnesium ammonium phosphate formed under the conditions of precipitation, contains more than a normal amount of magnesium, and that by dissolving the "white precipitate" in hydrochloric acid and reprecipitating,

and also by the presence of citric acid in the solution where the "white precipitate" is formed, the trouble is prevented.

H. Neubauer[1] has shown that magnesium ammonium phosphate formed in solutions containing an excess of both ammonia and magnesium salt, which is the condition of precipitation in the method under discussion, contains more than a normal amount of magnesium. The writer has had magnesium of the magnesia mixture to deposit as hydroxide and contaminate precipitates where very large excesses of the magnesia mixture were used in strongly alkaline solution and on long standing, though little or no error is thought to be introduced by this latter cause where the prescribed amount of magnesia mixture is used and too long standing not allowed. It is to the excess of magnesium in the magnesium ammonium phosphate, we consider, that the high results by the molybdate-magnesia method are due.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid" made by the writer to that association at its recent meeting.

N. C. Experiment Station,
Raleigh, N. C.

ON THE GUNNING METHOD FOR TOTAL NITROGEN IN FERTILIZERS.

By W. E. Garrigues.

Received September 28, 1894.

COMPARED to the Scovell-Kjeldahl nitrogen method, that of Gunning, modified to include nitrates, does not seem to have met with the favor that its cleanliness and simplicity would warrant. It is believed that this is, in the main, due to the lower results consequent upon the use of the latter process; hence the following record of an investigation of its merits.

The work was commenced by running parallel analyses on fertilizers of unknown composition, containing sodium nitrate, by both of the methods named. In each case the manipulation, adopted by the Association of Official Agricultural Chemists,

[1] Abstract *J. Chem. Soc.*, of London, October *1893*, 489.

was rigidly adhered to. The appended figures, being the results obtained, speak for themselves:

Kjeldahl with zinc dust. Per cent. nitrogen.	Gunning with sodium thiosulphate. Per cent. nitrogen.		
3.01	2.40	2.40	
4.98	4.30	4.35	4.55
3.53	3.00	3.10	3.24
4.02	3.50		
4.67	4.05	4.21	4.24

A sample was then prepared from pure sodium nitrate and tankage. The latter was valued by the plain Kjeldahl and Gunning methods and by soda-lime combustion, with the following results:

Kjeldahl.	Gunning.	Soda-lime.
7.05	7.05	7.08

The calculated content of the mixture was 8.97 per cent. nitrogen, about one-half of which was in the inorganic form. On submitting this to analysis there were obtained:

Kjeldahl.	Gunning.
8.90	7.17
....	7.31
....	7.46

It was very evident that in the writer's hands the Gunning method, as adopted by the Association, did not convert all the nitrogen present into ammonia. After numerous and varied experiments, which, as is usual when viewed in the light of foregone events, now seem to have been largely unnecessary; successful results were finally obtained by using the same reagents, both kind and quantity, but varying the mode and order of their addition.

For convenience of reference the official directions from Bulletin 38, U. S. Dept. of Agriculture, are here given:

"In a digestion flask holding from 250 to 500 cc. place from 0.7 to 2.8 grains of the substance to be analyzed according to the amount of nitrogen present. Ten grams of potassium sulphate, five grams of sodium thiosulphate, and thirty to thirty-five cc. of the salicylic acid mixture, *i. e.*, thirty cc. of sulphuric acid to one gram of salicylic acid, are then added and the whole digested at a low temperature until frothing ceases."

The above unsatisfactory, or rather useless, results were

obtained in this manner. The chief fault is in the addition of potassium sulphate at such an early stage in the process; the large quantity of dry powder forming an effectual blanket over the sample, that for some time resists the permeation of the viscid acid solution.

The best procedure was found to be: Adding the salicylic acid mixture directly to the sample in the flask, which is then shaken until the liquid has thoroughly wetted the dry organic matter, allow to stand about fifteen minutes, and add the thiosulphate with constant shaking. This should be done in four or five portions, following with a fresh crystal only when the one previously added has completely dissolved. The potassium sulphate is then put in and the whole again well agitated. Digest as usual.

Handled in this manner the known mixture above referred to, gave:

8.85
8.87
8.90
8.92

Another sample of dry bone tankage and sodium nitrate was prepared and passed several times through a sixty mesh sieve. The tankage was valued as before, and showed:

Kjeldahl.	Gunning.	Soda-lime.
4.32	4.32	4.39
4.40	4.42	

The calculated content of the mixture was 6.49, and the analyses returned:

Kjeldahl.	Gunning.
6.45	6.43
....	6.45
....	6.45
....	6.46

Neither method gave results sufficiently accurate for the valuation of sodium nitrate alone; a carefully prepared sample of that salt showing on analysis:

Kjeldahl.	Gunning.
16.05	15.80
16.35	16.00
....	16.15
....	16.22
....	16.38

Theory 16.49

It will be noticed that without a single exception the returns of analyses were below the amount actually present. No means of avoiding this loss were found. It would, therefore, seem justifiable to report the highest figure in closely agreeing duplicates instead of the customary average.

Several blanks run through to determine the freedom from nitrogen of the reagents employed, gave from nil to 0.05 per cent. No corrections were made for this.

During the distillation in the Gunning process the solution frequently foams badly; so much so that unless the flame is turned very low, the froth rises into the connecting bulb. The addition of paraffin wax does not always overcome this difficulty, and to avoid it, the use of an ordinary thirty-two-ounce wash-bottle, in place of the 500 to 600 cc. distillation flask is recommended.

There is little doubt that the seat of responsibility for many minor discrepancies is imperfect prepartion of the sample. Attendant upon the use of the official twenty-five mesh sieve, variations in the hands of the same manipulator frequently reach 0.15 per cent., even when exceptional care is exercised. It has, therefore, been found advisable in nitrated goods to quarter down the twenty-five mesh sample to about two ounces and pass that through a sixty mesh sieve; when this is done, the difference in duplicate analyses rarely exceeds 0.05 per cent., and decinormal acid and alkali often fail to show any.

Occasionally it becomes necessary to dry the sample before it can be thus finely powdered; in that case making the moisture determinations of Stillwell and Gladding (Bull. 38, p. 19, U. S. Dept. of Agr.) is the best procedure, *i. e.*, weigh out a portion of about ten grams from the original package when first opened, and determine the total moisture in a water-oven, dry the remainder of the sample to dustiness, and prepare it as above; then weigh out two grams of the fine sample simultaneously with the portion to be used for nitrogen, and ascertain the remaining moisture. A simple calculation brings the nitrogen figure back to the original condition of the goods.

Usually, however, nitrated fertilizers contain only a few per cent. of moisture, as indeed they should, lest the free acid of

the phosphate in the presence of water, act on the easily decomposable salt and liberate nitric acid. This theoretic action has been found a sad reality by manufacturers who incorporated nitrate salts with a wet "super," the loss of plant food being accompanied by a destruction of the fiber of the bagging containing the goods.

FALLACIES OF POST-MORTEM TESTS FOR MORPHINE.[1]

BY DAVID L. DAVOLL, JR.

Received August 9, 1894.

IN the qualitative investigations upon morphine in a former series of experiments, the tissue was allowed to putrefy in the open air, a condition which is not present in the case of a buried body, for in the unopened cadaver, the bacterial products are very different in their deportment toward certain reagents, from those formed by aerobic germs and are the interferences which would be met with in chemico-legal work and which give some of the tests for morphine.

The writer, during the spring of 1893, in a series of determinations to ascertain the minimum of loss entailed in the recovery of a weighed amount of commercial morphine sulphate—the form generally employed in instances of poisoning—from a given amount of putrefied tissue, obtained the following results by the method given in detail below:

A. From sixty grams of stale bread, containing 0.2387 gram of morphine sulphate, 0.0844 gram of anhydrous alkaloid were recovered, the equivalent of 0.2245 gram of morphine sulphate; this shows a loss of 0.0142 gram or 5.94 per cent. By qualitative tests upon $\frac{1}{500}$ part of this recovered amount, very decided affirmative results were obtained.

B. From 100 grams of fresh liver, containing 0.3455 gram of morphine sulphate, 0.1163 gram of anhydrous alkaloid were recovered, the equivalent of 0.3093 gram of morphine sulphate, a loss of 0.0362 gram.

C. From putrid liver (after standing ten days in the open air and in a warm place) charged, when fresh, with 0.442 gram of morphine sulphate, 0.111 gram of anhydrous alkaloid were

[1] Read at the Brooklyn Meeting of the American Association for the Advancement of Science, August, 1894.

recovered, corresponding to 0.2952 gram of morphine sulphate, a loss of 0.1468 gram.

After much experience with quantitative methods now in vogue, both in opium assay, and toxicological work I have used the method of titration of the alkaloid by standard acid and alkali, isolating the alkaloid by shaking out with primary amyl alcohol.

A careful review of the qualitative tests for morphine was first gone over, working with normal and decinormal solutions of the anhydrous alkaloid, in the form of sulphate. The figures here given, refer to the anhydrous alkaloid evaporated to dryness upon one spot in a porcelain dish.

Fröhde's Reagent.—See discussion below.

Iodic Acid, with starch paste, is sensitive to 0.00001 gram.[1]

Nitric Acid, gives deep orange color with 0.00001 gram. This reagent also produces a red coloration with certain volatile oils and resinous substances.

Ferric Chloride, in neutral solution gives deep blue color, said by Wormley to be sensitive to $\frac{1}{10000}$. Results with putrefactive tissue are given below by the writer.[2]

Ferric Chloride with *Potassium Ferricyanide*, is sensitive to 0.000005 gram.[3]

Tattersall's Test, with sodium arsenate, followed by other reagents, is very satisfactory. (For details, see "New Color Reaction for Morphine, Codeine, and Atropine," *Pharm. J. Trans.*, [3], **12**, 459–60.)

Many other tests were worked upon, but being for the most part confirmatory and quite intricate in their manipulation, they

[1] Blyth, 1885; Separation of Morphine from Animal Tissue and Fluids; Poisons, their Effects and Detection, 1, 278. Selvin has pointed out that amyl alcohol extracts from putrefied matters, "ptomaines," agreeing with morphine in setting free iodine from iodic acid.

[2] T. G. Wormley. 1885; Morphine, Micro-Chemistry of Poisons, second edition, 485-6, says "that the blue color produced by $FeCl_3$ upon morphine is discharged by free acids, caustic alkalies, and heat. The blue color may not make its appearance if foreign substances be present and it is open to fallacy."

[3] O. Hesse, Morphine, *Pharm. J. Trans.*, 18, 801, says, "In the ferric chloride and potassium ferricyanide test for morphine, the action is due to the formation of pseudomorphine and potassium ferrocyanide.

$8C_{17}H_{19}NO_3HCl + 8K_3Fe(CN)_6 = 4C_{34}H_{38}N_2O_6.2HCl + 6K_4Fe(CN)_6 + 2H_4Fe(CN)_6$.

Pseudo-morphine is actually deposited if the solution is not too dilute and this substance being somewhat soluble in water, is the cause of the blue coloration.".

were not applied in this work for reasons which the decisive results render obvious. The negative results in testing for morphine have always been regarded as more conclusive than the positive.

The object of this work was to demonstrate, as far as possible, to just what extent cadaveric alkaloids might respond to the generally recognized tests for morphine; and to this end, the ordinary manner of burial of a corpse was followed, and after exhumation the several parts of the body were subjected to exactly the same treatment that would be followed were morphine suspected to be present as a result of poisoning.

A collie (dog) was taken, weighing thirty-four avoirdupois pounds; was shot between the eyes on March 3rd, at 1.30 P. M. and placed in a tight pine-box, when the cover was screwed on. This was buried under five feet of soil, consisting of clay mixed with gravel, on the forenoon of March 5th. When buried, the body had already begun to give off a strong odor. The body was taken up on the morning of April 26th, after forty-five days burial, the usual spring weather intervening, the box being dry inside. Eight hours after disinterment, all the parts—portion of brain, heart, lung, kidney, liver, spleen, bladder and urine, stomach and contents, piece of intestine with contents—were separately macerating in diluted alcohol.

The weights of the several parts in grams were as follows: Brain, 45; heart, 173; lung, 200; kidney, 70; liver, 345; spleen, 28; bladder and urine, 105; stomach and contents, 450; intestine with contents, 130.

The odor from the opened cadaver was overpowering, particularly from the cranial cavity. All organs were soft, but retaining their form. The brain was of a semi-fluid consistence, and when, later, the liquid extract was shaken out with immiscible solvents it emulsified exceedingly.

The method of extraction, given below, includes some few modifications over the older method, none of which, however, were introduced without previous proof of their applicability to the recovery of the alkaloid, morphine. For convenience of reference in the following comments, the manipulation was divided into arbitrary stages, designated by Roman numerals.

I. The finely divided material is placed in a flask of suitable capacity, from which extends upward a glass tube, three and one-half feet long by one-fourth inch internal diameter; the arrangement provides for the constant alcoholic and acidulous strength during extraction, by air condensation. Enough diluted alcohol (by volume) is added to well cover the material and the mass made slightly acid with acetic acid. The digestion is made upon a long iron plate, heated by means of Bunsen burners, so placed, at intervals, that the flame should strike *between* the flasks and not *directly beneath* them. The flasks are placed in a row upon the hot plate, and further protected from direct heat of the iron plate by interposing match-sticks between the flask-bottom and the hot plate, and are virtually heated by hot air and not by the plate, the wood being such a non-conductor of the heat. The digestion is continued for one hour, the temperature, 70° C., being read from a thermometer immersed in the viscera. Then cool, remove to a funnel and filter through paper by means of a filter-pump, or strain through carefully washed muslin, rinsing the flask with successive small portions of diluted alcohol and passing washings through the tissue, previously well drained. Remove the mass to the extraction apparatus and repeat the process of extraction and filtration as before. Three extractions are accounted sufficient.

II. The alcohol is removed by evaporation upon the water-bath, stirring to promote vaporization and prevent the formation of a crust.

III. The measure of the residual aqueous liquid is now ascertained, and being of a sirupy consistence, is placed in a flask of suitable capacity and three volumes of ninety-five per cent. alcohol added; the evaporating dish is rinsed with seventy-five per cent. alcohol and the washings added to the liquid under analysis. Sulfuric acid, approximately fifty per cent., is added to slight acidulation and all is set aside for eight to twelve hours, agitating occasionally. It is then filtered by means of a filter pump, and the precipitate washed with successive small portions of seventy-five per cent. alcohol.

IV. Remove the alcohol from the filtrate by evaporation upon the water-bath, and dilute with just sufficient water to obtain a

limpid consistence. The presence of much fatty matter may necessitate filtration; maintain the acid reaction.

V. The acidulous solution is now shaken with successive small portions of water-washed chloroform, until, upon evaporation, the chloroform solution leaves no appreciable residue; the miscibility of the so-called immiscible solvents causes a slight residue to remain upon evaporation, even after the chloroform has performed its work.

VI. Now shake out the acidulous solution with a cold amyl alcohol. These two solvents (V and VI) remove coloring and fatty matter. The chloroform and amyl alcohol washings should be shaken with slightly acidulated water and this latter added to the original liquid under analysis.

VII. The liquid is now made alkaline with ammonia water of sp. gr. 0.962 at 15° C. and shaken out with several successive small portions of chloroform and ether (three parts to one), this to remove cadaveric alkaloids as much as possible; this was suggested by the solubility of the cadaveric alkaloids in these media and the insolubility of the morphine in the same. This is repeated four times, the aqueous liquid being each time acidulated, the immiscible solvent added, shaken, and again rendered alkaline before the solvent has time to separate into a layer; this is done in order to obtain the alkaloids nascent.

VIII. (*a*) The same conditions of acidulating, adding hot solvent and making alkaline were observed here as in "Stage VII." The suspected (acid) is heated to 70° C., placed while hot in a separatory-funnel, and when alkaline, shaken out with successive small portions of hot amyl alcohol, until a small portion, upon evaporation, gives negative results with some delicate test, three to five shakings being generally enough.

(*b*) The amyl alcohol solutions are mixed, filtered, and then shaken with successive very small portions of water until no precipitate is afforded with barium chloride.

IX. It is then evaporated to dryness upon the water-bath and the residue taken up with slightly acidulated water, fiftieth normal sulphuric acid being the strength employed.

X. Filter this liquid, heat to 70° C., and shake with two successive portions of hot amyl alcohol in *acid* solution, mixing the

amyl alcohol washings and agitating with a little acidulated water, which is added to the liquid under analysis. This is done to further remove coloring matter. See remarks further on.

XI. Heat again to 70° C., add hot amyl alcohol, shake, render alkaline with ammonia water (0.962), again agitate and remove the amyl alcohol solution; repeat this extraction with hot amyl alcohol until all the alkaloid has been removed. Now repeat the shaking with water, as mentioned in "Stage VIII (*b*)" in order to remove ammonium sulphate.

XII. Four-fifths of the final purified amyl alcohol solution are evaporated to dryness upon the water-bath and titrated with fiftieth normal potassium hydroxide and sulphuric acid, using cochineal solution as indicator. The remaining one-fifth is tested qualitatively by all reliable methods.

The above is a detailed account of the method of extraction.

Guareschi and Mosso found commercial alcohol almost invariably to contain small quantities of an alkaloidal substance, having an odor similar to that of nicotine and pyridine. In amyl alcohol, Haitinger has found as much as one-half per cent. of pyridine. The ethyl alcohol and primary amyl alcohol used in this investigation were purified by distillation over tartaric acid, using five grams of acid to each 100 cc. of alcohol, the distillates coming over at 78° and 130° respectively. The basic substance which exists in some samples of ether is pyridine. The ether was water-washed, dried over calcium chloride and redistilled. Ether containing alcohol, as is well known, has a tendency to remove morphine from alkaline media. The chloroform was water-washed and redistilled. None of the above enumerated solvents, upon evaporation of fifty cc., yielded any appreciable residue, and upon applying reagents for morphine to the spot upon which the evaporation had been made, entirely negative results were obtained. "Stage VI" was omitted in extraction of all parts, excepting with liver, kidney, and intestines, since it was thought that, as morphine is removed from acid solution by amyl alcohol, it would be advisable to first purify the alkaloid by stages VII and VIII, thus leaving much coloring and extractive matter behind, and then to shake out the *hot* acid solution with successive portions of hot amyl alcohol, where a less amount

of the solvent need be employed and at the same time the very objectionable coloring matter would be more thoroughly removed. It was noticed in "Stage VI" that the *cold* amyl alcohol removed very little coloring matter, but that this same solvent, when *hot*, removed very much in "Stage VIII," which is avoided in "Stage XI." The reason why this method was not employed in the cases of the liver, kidney, and intestines, was that the idea did not suggest itself until after the final tests were applied to these. Before making this departure from the usual method the feasibility of it was first to be ascertained by actual experiment. One-half the final purified extractive matter from the liver was taken, in which negative tests for morphine had been obtained by Fröhde's reagent, Le Fort's test, and ferric chloride. Into this extract was introduced 0.0006 gram of morphine and all evaporated to dryness upon the water-bath; taken up with 100 cc. of fiftieth normal sulphuric acid, and this *hot* solution (acid) shaken out with twenty-five cc. of hot amyl alcohol. The solution was now shaken out with successive portions of twenty-five, twenty, and twenty cc. of *hot* amyl alcohol in alkaline media. The final measure was sixty cc. of purified amyl solution, each cubic centimeter of which *could not* contain more than 0.00001 gram of morphine. One cc. of this solution evaporated to dryness upon one spot gave very decided tests for morphine by Fröhde's reagent, which was the only test applied to the only perceptibly yellow residue. This test was as pronounced and strong as from 0.00001 gram of morphine evaporated from aqueous solution.

The stomach and heart yielded an extract of a very dark color, but by subsequent purification, particularly at "Stage IX," it was reduced to a very pale yellow, and, in fact, all extractive matter was freed from almost all color at this point, as the fiftieth normal sulphuric acid failed to appreciably effect the dark residue left at this stage. This residue needs some further mention; it was brownish to black in color, somewhat resinous and plastic in consistence; when not abundant it appeared as a brownish cryptocrystalline residue, taken up to a considerable extent by the fiftieth normal sulphuric acid. By computation it will be seen that 100 cc. of fiftieth normal sul-

phuric acid is capable of saturating 0.57 gram of anhydrous morphine, $C_{17}H_{19}NO_3$; or 0.606 gram of crystallized alkaloidal morphine, $C_{17}H_{19}NO_3,H_2O$, corresponding to 1.516 grams of morphine sulphate, $(C_{17}H_{19}NO_3)_2H_2SO_4.5H_2O$.

After treating with fiftieth normal sulphuric acid the solution is filtered through paper.

The final purified solution treated as above, is almost colorless at "Stage XII," and the residue left upon evaporation was, in the case of the brain, almost colorless: light yellow with all others, excepting the heart and stomach, which were yellow to light-brown.

The filtered liquid, after performing "Stage IX," was tested for alkaloids by bromine water, Wagner's solution, Mayer's reagent, sodium phosphomolybdate, and picric acid and all parts of the viscera gave strong precipitates with each reagent, excepting picric acid. The cautious addition of ammonia water to them also gave cloudiness.[1]

The reagents for the final identification tests were prepared for the most part after the directions given in "Reactions" by F. A. Flückiger, translated, revised, and enlarged by J. B. Nagelvoort.[2] Fröhde's reagent was made of the strength 0.010 gram of molybdic acid to each cubic centimeter of sulphuric acid, sp. gr. 1.84, and dissolved by digesting below 150° C.

The nitric acid test, ferric chloride with potassium ferricyanide, and the ferric chloride test were of the above recognized strength (Flückiger).

Le Fort's test was applied as follows: Iodic acid in solution is applied to the dry residue and all intimately mixed; chloroform, in successive small portions, is floated over this until it ceases to remove the pink color of iodine, the chloroform solution being removed by absorption with filter paper; one drop of ten per cent. ammonia water (or until alkaline) is now added and morphine will give a deep "mahogany color" not affected

[1] For a discussion of the production of precipitates with organic matter by such general alkaloidal reagents as Wagner's solution, Mayer's reagent, bromine water and picric acid. See T. G. Wormley, 1885; Morphine, Micro-Chemistry of Poisons, second edition, 492.

[2] Schönn, *Ztschr. anal. Chem.*, 8, (*1869*), 379., in regard to preparing Fröhde's reagent says: "A moderate heat only should be applied, since the molybdic acid is reduced to a blue precipitate by heat alone at the temperature of incipient vaporization of H_2SO_4."

by chloroform, but changing back to yellow with hydrochloric acid. 0.00001 gram of pure morphine will respond to this test but the writer would not claim such extreme delicacy of reaction in presence of foreign matter; 0.00005 gram gives a good decided test, suitable for recognition in recovered matter.

After somewhat extended work upon morphine in the viscera, it seems to me that under the conditions mentioned, Fröhde's reagent, Le Fort's test, and ferric chloride are the least fallacious of all recognized tests applied.

Fröhde's reagent is especially satisfactory, appearing immediately as a deep purple color, fading to violet, then green, when applied to extractive matter *known* to contain morphine, and under these conditions sensitive to 0.00001 gram. In applying this test two samples, each containing extract from two cc. of the purified amyl alcohol solution were evaporated upon one spot in a porcelain dish upon the water-bath; to one of them was first added, and intimately mixed, 0.00001 gram of alkaloid morphine; the test was applied to both samples at the *same time* and in no instance was there obtained any indications whatsoever of morphine in the sample of extract *not* containing that alkaloid, a light green color only, appearing; but, on the other hand, the sample to which 0.00001 gram of morphine *had* been added, never failed to give a decided purple color *immediately*. These parallel tests were made for the purpose of verifying the conclusion, that, had morphine (or an alkaloidal base acting similarly toward Fröhde's reagent) been present in even so small an amount as 0.00001 gram a reliable test would have been obtained.

With ferric chloride, freshly dissolved and free from acid, the same parallel tests were made as with Fröhde's reagent, with the exception that 0.00005 gram of morphine was introduced in the comparative test, since this test is not as delicate as the molybdate in extractive matter. When applied to the extractive to which morphine had been added, bluish rings appeared, a positive test; but with the pure extract, from all parts of the viscera, no color appeared.

Le Fort's test was applied with a parallel test, containing 0.00005 gram of morphine and was very satisfactory as a reagent,

and as far as demonstrating the absence of morphine or any interfering bases was concerned, was conclusive. With the extractive to which morphine *had* been added, a final "mahogany color" had been obtained, but no change with the pure extract from the parts of the body.

Iodic acid gave indications of a reducing agency, since iodine could be detected with clear, fresh starch-paste in all instances.

The nitric acid tests were found to be of no value, ferric chloride, with freshly prepared solution of potassium ferricyanide, gave indications of a base having similar reducing action as morphine. Parallel tests were made, the one containing the extractive from two cc. of final amyl alcohol solution, was evaporated to dryness, taken up with four cc. of fiftieth normal sulphuric acid; the other treated in an exactly similar way, *but* to which had been added 0.00001 gram of morphine. To both these solutions were added eight cc. of a solution of potassium ferricyanide and one drop of solution of ferric chloride. With the portion known to contain morphine, a blue color appeared *at once;* with the simple extractive matter from the viscera, only a light green color appeared, not changing at all in three minutes; slightly darker in five minutes; after ten minutes one could easily distinguish the samples one from the other, but after two hours both had deposited a similar blue precipitate.

During the process of extraction of the different organs, it was noticed that from them, and particularly from the liver, brain, spleen, intestines, and kidney, a decided odor resembling that of trimethylamine was given off, continuing all the way through.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June 2, 1894.

FERMENTATION OF GLUCOSE SYRUPS.

BY HORACE E. HORTON.

Received October 23, 1894.

I WOULD like to call attention to the interesting fact that glucose syrup of 41° Bé. is fermentable. The opinion is general that glucose of this gravity is non-fermentable and I am unable to find any published record of such fermentation.

During the summer of 1893 large quantities of the so-called "mixing glucose" sold in southern cities was found to be in a

state of active fermentation. It was thought that the samples were of light gravity, but moisture determinations showed 21.1 per cent., the normal quantity for 41° Bé. syrup. This fermentation was found to exist not alone in the 41° syrup but in samples of 42° Bé. containing 20.19 per cent. moisture.

Cultures of the various liquors in the refinery showed that the ferment was introduced into the goods at some point after the 39° Bé. vacuum pan.

To prevent the finished goods from fermenting the following experiments were made with well-known antiseptic materials.

1.46 pounds of 40° Bé. sodium bisulphite added to each barrel of fifty-two gallons. No effect.

One-half ounce boracic acid and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

1.46 pounds of 40° Bé. sodium bisulphite, one-half ounce boracic acid, and one-quarter ounce benzoic acid to each barrel of fifty-two gallons. No effect.

TOPEKA, KANSAS, October, 1894.

ON THE TECHNICAL ANALYSIS OF ASPHALTUM.

BY LAURA A. LINTON.

Received September 21, 1894.

IN the year 1837, J. B. Boussingault published his celebrated memoir on the "Composition of Bitumens." In the researches upon which this memoir was based he had discovered that certain bitumens yielded to one class of solvents a portion of their content and to another class of solvents another portion of their constituent hydrocarbons. He called the first portion "Petrolene" and the second portion, "Asphaltene."[1]

In 1827[2] Le Bel and Muntz went over the same ground and in 1883 Le Bel again went over it, adding a few facts in relation to other bitumens than those previously examined but leaving the two substances, petrolene and asphaltene, practically where he found them.[3]

In 1837 the conclusions based on chemical research were far less exact than at the present time and Boussingault concluded that the substances, petrolene and asphaltene, were simple sub-

[1] *Annales de Chemie et de Physique*, 64, 141.
[2] *Bull. Soc. Chim.*, 17, 156. [3] Ibid, 50, 359.

stances and also that they were identical from whatever sources they were derived. In this conclusion Le Bel in a measure appears to coincide.

It, however, requires no argument to prove, to any one at all familiar with the subject, that petrolene is nothing but a name that covers a great variety of substances, radically unlike, that exist in different forms of bitumen and are only related, in this instance, as being held in solution by a certain limited number of menstrua and which include the whole list of paraffines and iso-paraffines, the olefines, the benzenes and additive benzenes with many other less abundant and well-known substances.

Ethyl ether and so-called petroleum naphtha, which latter is an indefinite mixture of fluid paraffines and iso-paraffines of high specific gravity, are the solvents used; but no determination has been made as to the influence of proportion in the mixtures of the substances dissolved, or as to the relative solvent powers of the two menstrua upon the different constituents of these mixtures. In fact petrolene is nothing but a name which at present covers a vast expanse of the unknown.

It can be safely said that probability favors the assumption that asphaltene is a little more definite; but no certainty attaches to the identity of asphaltene from different sources or of asphaltene dissolved by different menstrua.

Therefore, in a general way, it may be said that asphaltene is that portion of the different forms of bitumen that is soluble in carbon disulphide, chloroform, benzene and a few other less well-known liquids and is not soluble in the menstrua that dissolve petrolene.

As the bitumens examined by the French chemists, above mentioned, have never assumed commercial importance, the questions relating to petrolene and asphaltene have remained matters of scientific interest only. However, since asphalt paving has become a business involving the expenditure of large sums of money these problems are beginning to assume a wide importance outside the laboratory of the chemist and to demand from technologists very serious consideration. Within recent years large numbers of so-called analyses have been reported, which represent various attempts to determine and set forth the rela-

tive value of many samples and kinds of asphaltum, that may or may not be suitable for the many uses to which asphaltum is applied, but more particularly with reference to street paving. Prominent among the chemists who have been more or less extensively engaged in these analyses of asphalts are Mr. Clifford Richardson, Dr. Henry Leffmann, Dr. Samuel P. Sadtler, and Dr. De Smedt.

A perusal of the numerous published reports of Mr. Richardson reveals the fact that in his tests the solvents used for the extraction of petrolene and asphaltene, were petroleum ether and carbon disulphide, while Drs. Leffmann and Sadtler, in their investigations and tests of asphalts, used alcohol—presumably ethyl-alcohol—carbon disulphide, and ether as shown by the report submitted to the Citizens' Municipal Association and the Trades League of Philadelphia.

Neither of these gentlemen describe any process or method employed in obtaining the results stated. It is hardly consistent with the nature of the reports that they should. Nor has Mr. Richardson, in an article published in the *Journal of Analytical and Applied Chemistry*, in the numbers for December, 1892, and January, 1893, given any detailed description of the process he employed in order to obtain the numerous results of analysis that he there uses.

But little satisfaction can be derived from consulting Allen's encyclopedic work so exhaustive upon every subject relating to technical organic analysis.[1]

We find therein the following statements and notes concerning the solvents and methods used in the analysis of asphalts: "For the determination of the *total bituminous matters* in asphalt rock and mixtures containing it, C. T. Kingzett extracts the air-dried sample with freshly distilled Russian oil of turpentine, evaporates (*Analyst* **8**, 4) the resultant solution and weighs the residue. The matter insoluble in turpentine is washed with ether, the *calcium* and *magnesium* carbonates dissolved in hydrochloric acid and the washed insoluble *siliceous matter* weighed."

"H. P. Cooper prefers carbon disulphide for dissolving out the bituminous matters from asphaltic mixtures."

[1] Commercial Organic Analysis, by Alfred H. Allen, London, *1886*, 2, 375, 376, 377.

Allen adds in a note, "The carbon disulphide employed for dissolving the bituminous matter must not contain free sulphur. It may be replaced by chloroform or benzene (coal tar naphtha). If the residue left after extraction be dark colored, foreign organic matters of valueless nature are present. Their proportion may be determined by igniting the weighed residue left after dissolving out the asphaltum, recarbonating it with ammonium carbonate, again gently heating it and reweighing. The loss of weight is the amount of *non-bituminous* organic matter present. In the case of samples leaving a white residue after exhaustion with carbon disulphide, the bituminous matter may be simply and accurately ascertained from the loss on ignition, taking care to recarbonate the lime before weighing."

In another note, page 377, he says: "Five grams of the finely divided sample were digested for one hour with fifty cc. of petroleum spirit (sp. gr. 0.7) and the mixture frequently agitated. The liquid is then boiled for a short time, decanted and the residue boiled with another quantity of twenty-five cc. of petroleum spirit. This treatment is repeated eight or ten times until the exhaustion is complete.

"E. Davies (*Pharm. Jour.*, [3], **14**, 394), reports that none of the organic matter in Val de Travers asphalt is insoluble in petroleum spirit."

Now, when we take into consideration the fact that turpentine, carbon disulphide, ether, chloroform, and benzene have been used indiscriminately by chemists in the extraction of asphaltene, the question very naturally arises are the results that have been and that are being obtained by these different methods of analysis strictly comparable—that is, are they convertible terms? Will the same asphalt treated with different solvents show in each case the same percentage composition? If not, then it is evident that asphalt taken from different localities and subjected to dissimilar methods of analysis cannot yield results of any value so far as purposes of comparison are concerned. Then again, if turpentine, carbon disulphide, and chloroform give a different proportion of asphaltene in the same asphalt it is just as evident that asphaltene, instead of being a definite

chemical substance, is a mixture, which mixture would doubtless vary in different asphalts.

It was for the purpose of determining whether petroleum ether (paraffines), California naphtha, and ethyl ether are interchangeable solvents of petrolene and whether turpentine, carbon disulphide and chloroform are interchangeable solvents of asphaltene that the research, the results of which are here given, was undertaken. That a series of such tests, faithfully carried out, should lead to the establishment of a method of analysis applicable to all asphalts and, at the same time, reveal something regarding the real nature of petrolene and asphaltene was inevitable.

The specimens analyzed were furnished me by Prof. S. F. Peckham, Chemist of the Union Oil Company of California, and were as follows:

1. *Crude Trinidad Asphaltum.*—From the Warren-Scharf Asphalt Company, of New York City. This specimen contained little or no water, as, for several months, it had been broken in small pieces, and so had lost the water which this asphaltum generally contains.

2. *Cuban Asphalt.*—A commercial sample obtained in New York City.

3. *Kuban Residuum.*—An artificial asphalt obtained from the distillation of Kuban petroleum from the western extremity of the Caucasus Mountains, Russia.

4. *Egyptian Asphalt.*—An Assyrian asphalt taken from the Dead Sea and imported into Egypt. This specimen was obtained in New York City.

5. *Asphaltic Rock.*—From Val de Travers, Switzerland. This asphalt was a sample of natural rock obtained at the office of Wm. H. Delano, representative of the French Company in New York City.

6. *Seyssel Asphaltic Rock.*—From the well-known locality in eastern France, obtained from the same source as No. 5.

7. *Turrellite.*—From a deposit lately discovered in Uvalde County, Texas, consisting of a mass of sea-shells cemented together by bitumen into a solid rock mass. It occurs in a rock formation said to be of Jurassic age, in which formation the Val de Travers rock also occurs. This specimen was obtained from

the office of the Litho-carbon Company of New York City.

8. *Kentucky Asphaltic Rock.*—Obtained from Marshall Morris, Esq., Louisville, Ky.

9. *An Asphaltic Mineral.*—Resembling Gilsonite; reported as coming from Utah.

10. *California Maltha.*—Taken from a well at Summerland, on the coast, near Santa Barbara.

11. *Asphaltum.*—From mines recently opened near Asphalto, Kern County, California, in the eastern foot hills of the Coast Range Mountains, about thirty miles west of Bakersfield.

12. *Asphaltic Sandstone.*—From San Luis Obispo, California.

13. *Asphaltum.*—Picked up on the beach at San Buena Ventura, California, washed in from the Santa Barbara channel.

14. *Asphaltum.*—From the Ojai ranch, Ventura County, California.

15. *Grahamite.*—A so-called asphaltum taken from a vein in Ritchie County, West Virginia.

16. A portion of a compressed brick made from the asphaltic rock taken from the Seyssel mines. Exhibited at the Columbian Exposition.

17. *Hard Artificial Asphalt.*—An asphaltic residue obtained from the distillation of petroleum obtained near Santa Paula, California. It is known in the refinery of the Union Oil Company, of California, as grade "B."

18. *Soft Artificial Asphalt.*—From the refinery of the Union Oil Company, of California, at Santa Paula. Grade "D."

19. *Asphaltic Pavement.*—Obtained from Franklin Avenue, Buffalo, N. Y. It was laid in 1878, of Trinidad asphalt, wax tailings, and very fine sand. It is remarkable as having been laid for fifteen years with almost no need of repairs.

20. *Asphaltic Pavement.*—From Governor's Island, New York Harbor, laid within the Fort at an unknown date, but so old that it has begun to break up from natural causes. Obtained from J. A. W. Pine, of New York City.

21. *Dubb's Artificial Asphalt.*—A so-called asphaltum obtained in operating the Dubb's patent process for the manufacture of asphaltum by adding sulphur to hot Lima-tar and thereby burn-

ing out the hydrogen. This is an asphalt only in name. The specimen was obtained from J. A. W. Pine, of New York City.

22. *Roofing Pitch.*—Obtained from the Mica-asphalt Company, of New York City.

23. *Pitch.*—Obtained as a residuum in the distillation of Scotch blast-furnace tar. This specimen was obtained from the same source as Nos. 20 and 21.

In making tests to determine the best method to be used in the analysis of asphalts the well-known Trinidad and Cuban asphalts were used and all analyses were made in duplicate. In the case of asphalts rich in bituminous matter about a half gram of the material, finely powdered, was used but in the case of asphalts in which the mineral matter constituted a large proportion the quantity was increased to several grams.

The sample was weighed in an Erlenmeyer flask and digested over night in about fifty cc. of petroleum ether; in the morning the clear solution, containing the dissolved petrolene, was passed through a balanced filter and a fresh portion of petroleum ether added to the contents of the flask. The second digestion was continued for two or three hours when the solution, as before, was filtered off and the process repeated until the whole of the petrolene had been removed. The contents of the flask were then thrown upon the filter and thoroughly washed with petroleum ether. Cold turpentine was then poured upon the filter in successive portions until the filtrate passed through colorless when the assumption was made that all the asphaltene and consequently all the bituminous matter had been removed.

The remaining organic matter, not bituminous, was determined by difference, that is, the residue on the filter, after digestion in turpentine, was washed with ethyl alcohol, dried, and weighed in order to determine the percentage of asphaltene after which the residue was burned in a platinum crucible, the difference in weight representing the organic matter not bituminous.

The contents of the crucible were now purely inorganic and, in the case of most asphalts, the residuum was sand more or less colored with iron.

The analysis of Trinidad asphalt under this treatment gave so low a percentage of asphaltene and so large a proportion of

organic matter not bitumen, that it was clearly evident that *cold* turpentine had not dissolved, and could not dissolve all of the asphaltene.

A second set of experiments was then tried in which cold turpentine and carbon disulphide were used as solvents of asphaltene. The results obtained for samples 1 and 2 were as follows:

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	32.54	20.3435	12.368	34.6775	99.929
" 2.....	25.049	54.53	2.441	17.9215	99.9415

The experiment was now made of somewhat varying the method of treatment for the following reasons: First, because of the difficulty of dissolving out the asphaltene while on the filter by simply allowing the solvent to run through it, and secondly, because, in consequence of the high specific gravity of petroleum ether, a considerable portion of sand or other mineral matter, mixed with asphaltene, always adhered to the flask, thus necessitating a separate determination of this portion. The method now employed for the removal of petrolene and asphaltene was the decantation method, and the solvents used for asphaltene were hot turpentine and chloroform.

The samples were digested over night in petroleum ether; in the morning the solution containing the petrolene was, as far as practicable, removed from the flask and the remainder was evaporated over a steam-bath; after weighing, the residuum containing the asphaltene was digested in hot turpentine over the steam-bath, and finally, the whole contents of the flask were poured upon a balanced filter and treated as in the first experiments.

The percentage composition of Nos. 1, 2, and 17, as determined by the decantation method, was as shown in the following table:

Sample.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	31.51	22.9865	11.4195	34.073	99.989
" 2.....	25.055	52.245	5.758	16.918	99.962
" 17.....	64.571	21.2545	13.706	0.3613	99.8928

In carrying out this method a great many determinations were lost, due to the fact that, in evaporation to dryness over the steam-bath, the contents of the flask were in part bumped out. In consequence, this method was soon abandoned as impractica-

ble, and finally, funnels with stop-cocks were employed, in which the contents of the filter could be digested. Boiling hot instead of cold turpentine was used, and, when necessary, the digestion was continued over night, and all the after washings were made with hot turpentine. Numerous trials showed that carbon disulphide dissolves little more than hot turpentine. The last trace of asphaltene, insoluble in either turpentine or carbon disulphide, was removed by chloroform.

In order to determine the relative solvent power of hot turpentine, carbon disulphide, and chloroform, the following method of qualitative analysis was applied to the twenty-three samples enumerated above. From a half gram to one gram of the material was digested over night in a four-ounce Erlenmeyer flask with about fifty cc. of petroleum ether. Next morning the contents of the flask were poured upon a filter, and the undissolved residue washed with petroleum ether until the filtrate was no longer colored. Boiling spirits of turpentine was then poured upon the filter until it passed through colorless, when carbon disulphide was used in the same manner, followed lastly by chloroform. The action of the successive solvents is shown in the following table:

Sample.	Hot turpentine.	Carbon disulphide.	Chloroform.
No. 1.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 2.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a perceptible amount.
" 3.	Dissolves nearly all.	Dissolves a trace.	Dissolves a trace.
" 4.	" " "	" the slightest trace.	" the slightest trace.
" 5.	" " "	Dissolves a trace.	Dissolves a perceptible amount.
" 6.	" " "	" "	Dissolves a perceptible amount.
" 7.	" " "	" the slightest trace.	Dissolves the slightest trace.
" 8.	" " "	Dissolves the slightest trace.	Dissolves a trace.
" 9.	" nothing.	Dissolves nothing.	" "
" 10.	" nearly all.	" a trace.	" a perceptible amount.
" 11.	" " "	" "	Dissolves a perceptible amount.

Sample.	Hot turpentine.	Carbon disulphide.	Chloroform.
No. 12.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 13.	" " "	" "	Dissolves a perceptible amount.
" 14.	" " "	" "	Dissolves a perceptible amount.
" 15.	" a large amount.	" a considerable amount.	Dissolves a considerable amount.
" 16.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 17.	" a large amount.	" a considerable amount.	Dissolves a considerable amount.
" 18.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.
" 19.	Dissolves nearly all.	Dissolves a trace.	Dissolves a perceptible amount.
" 20.	" " "	" "	Dissolves a perceptible amount.
" 21.	" " "	" "	Dissolves a trace.
" 22.	" a large amount.	" a considerable amount.	" "
" 23.	Dissolves a large amount.	Dissolves a considerable amount.	Dissolves a considerable amount.

Of the twenty-three asphalts examined, there was not one that did not yield some asphaltene on treatment with chloroform; consequently, it is safe to infer that in the analysis of asphalts, unless final washing be made with chloroform, the per cent. of asphaltene will be too low. There was a marked difference observed in the different asphalts as to the manner in which their constituent asphaltene was dissolved on treatment with hot turpentine. In Nos. 4, 5, 6, and 7, and a few others, the asphaltene dissolved out in a few minutes, while in the case of others, notably No. 15, it was a matter of hours, and even of days, before every trace soluble in turpentine could be removed. No. 9 seems to be an asphaltic freak as it contains no petrolene whatever and is insoluble in both hot turpentine and carbon disulphide, while chloroform and amylic alcohol dissolve but the slightest trace.

It was a difficult matter to determine the relative quantity of asphaltene dissolved by the different menstrua, as the only guide used was the color of the filtrate. This suggests a most

interesting research—the fractional, quantitative determination of asphaltene.

From my experience in the analysis of asphalts, I would advise that a preliminary qualitative analysis be always made of each new variety of asphaltum before any quantitative determinations are attempted, care being taken to observe the behavior of different asphalts with the different solvents. This method of procedure is to be recommended, not only because it would prove an economy of time and reagents used, but also because, in this way, much would be learned concerning the nature of petrolene and asphaltene.

A trial was made with Cuban asphalt to determine the solvent power of petroleum ether (87° Beaumé) as compared with that of California naphtha (74° Beaumé) and ethyl ether with the following results:

Sample.	Solvent for petrolene.	Per cent. of petrolene.
No. 2.	Petroleum ether	25.8516
" "	California naphtha	32.444
" "	Ethyl ether	32.5455

The high percentage of petrolene when California naphtha or ethyl ether are used indicates that the asphaltene is, in part, dissolved, and consequently, that these menstrua can not be used as solvents of petrolene in the determination of asphalts.

In selecting a method for the quantitative analysis based upon the results of these experiments, it is assumed that, until a strictly scientific method is worked out, the present empirical determination of petrolene and asphaltene will continue in use. The three considerations of economy, speed, and convenience, will together control the selection. So long as the significance of the difference between the 25.8 per cent. dissolved by petroleum ether and the 32.5 per cent. dissolved by ethyl ether is an unknown element in the problem—that is, whether it be seven per cent. of petrolene or of asphaltene that is involved—it is better to use petroleum ether, because it is cheap and easily obtained of a uniform quality. So, too, it is better to use boiling hot turpentine followed by chloroform as solvents of asphaltene, and thus rid ourselves of carbon disulphide altogether.

With these considerations in view the following method of analysis is recommended:

Weigh two suitable portions in four-ounce Erlenmeyer flasks, add fifty cc. of petroleum ether, cover, and allow to stand over night. The following morning decant the liquid upon a balanced filter placed within a three-inch funnel provided with a stop-cock in the neck. Add another portion of petroleum ether to the flask, allowing two or three hours for digestion, and decant the liquid upon the same filter as before; this process is to be continued until the liquid ceases to be colored, then transfer the whole of the bitumen to the filter. Dry the flask in a steam-bath and weigh; any increase in weight of the flask should be subtracted from the amount determined as petrolene. Wash the filter and its contents with petroleum ether, place these with the filter counterpoise in a steam-bath, dry, and weigh; the loss in weight of the bitumen represents the petrolene.

Rinse the flask thoroughly with boiling turpentine and add the liquid to the filter in the closed funnel, pour upon the filter a sufficient quantity of boiling turpentine to wholly submerge it, cover and allow the digestion to continue for several hours or over night. Repeat the digesting and filtering with boiling turpentine until the filtrate becomes colorless. The filter should be much smaller than the funnel. Rinse the flask with chloroform and pour upon the filter, add sufficient chloroform to wholly submerge the filter and allow at least an hour for digestion; wash with chloroform until the filtrate passes through colorless, then dry and weigh; the loss in weight represents the asphaltene. The filter is now to be burned in a platinum crucible and, if the asphaltum be combined with limestone, the residue recarbonated with ammonium carbonate, dried in a steam-bath, and weighed, the loss in weight represents the organic matter not bitumen, or coke, in the case of artificial asphaltic residuum, produced by heat.

There is necessity for washing the flask with the different solvents, not only because the petroleum ether is too light to rinse out all of the mineral matter, but also because some of the asphaltene adheres to the flask. Generally the turpentine removes all of the mineral matter, as well as part of the asphaltene, but if it does not, then after the flask is rinsed with chloroform it must be again dried and weighed and the increase in weight added to

the weight of the mineral matter in the platinum crucible. If water be present the asphalt should be dried in a steam-bath to a constant weight before being digested in petroleum ether. It is possible that some natural asphalts might experience a trifling loss of volatile oils at the temperature of the steam-bath, but in most instances such loss would be too slight to be regarded. With care and patience this method has been found capable of yielding very closely concordant duplicate results at each step.

The following table exhibits the results of a number of quantitative analyses made according to this method.

Sample.	Water.	Petrolene.	Asphaltene.	Other organic matter.	Mineral matter.	Total.
No. 1.....	2.029	32.4455	22.1115	8.1215	35.2865	99.994
" 2.....	0.3911	25.4605	54.414	2.469	17.0305	99.7651
" 4.....		35.087	63.183	1.7285		99.9985
				Not recarbonated.		
" 5.....		8.518	3.924	25.791	61.764	99.997
" 6.....		7.486	4.316		88.198	100.
" 7.....		8.786	3.267		87.947	100.
" 8.....		3.349	2.4215		94.228	99.9985
" 12.....	0.335	11.323	3.81	1.124	83.407	99.999
" 15.....		49.959	50.041			100.
" 17.....		64.571	21.2545	13.706	0.3613	99.8928
" 18.....		63.498	29.966	6.095		99.559
" 19.....		4.387	2.831	4.102	88.65	99.97
" 20.....	0.434	6.666	1.87	3.697	87.33	99.997
" 21.....		66.788	31.932	1.278		99.998

While this research is in no sense complete—it has in fact but opened up a wide field for further work—yet, sufficient evidence has been obtained to show that petrolene and asphaltene are not substances, but empirical terms that designate mixtures of substances soluble under certain conditions in different menstrua.

It is not unfair to assume that in these empirical mixtures, so long known under the names of petrolene and asphaltene, the lower members of all the different groups of hydrocarbons now known may be found. Again—just as some petroleums, which are varieties of bitumen, consist chiefly of paraffines—notably Pennsylvania petroleum—and some, like Russian petroleum, consist of the additive benzenes, while still others contain mixtures of the two is it not reasonable to presume that solid bitumens, like liquid bitumens, are equally variable in composition?

If this be the case, then it is equally fair to assume that any solvent taken will not dissolve substances of identical composition from different asphalts.

A review of the results here given suggests the query, have the methods heretofore employed for the technical analysis of asphaltum really been analytical at all? Would not a method and process suggested by the results of the qualitative analyses given in this paper and based on the successive application of different solvents and yielding results similar to those of fractional distillation really become analytical, especially if the separate portions dissolved by the different solvents were subjected to such treatment by oxidizing agents as would enable us by a comparison of the products of oxidation to determine to what groups of hydrocarbons the different substances dissolved respectively belong?

I take pleasure in hereby acknowledging my indebtedness to the courtesy of Hon. Thos. R. Bard, President of the Union Oil Co., of California, for the use of the laboratory of the company while engaged in this research.

MINNEAPOLIS, MINN., Sept. 16, 1894.

ACTION OF METALLIC MAGNESIUM UPON MANGANOUS SALTS.

BY JOS. G. HIBBS AND EDGAR F. SMITH.

Received June 18, 1894.

THE statements relating to the action of metallic magnesium upon solutions of manganous salts are contradictory; thus Manck (Ueber d. Verh. d. Magnesium und Aluminum gegen Salzlösungen, Goettingen, *1862*) states that metallic manganese is readily precipitated by magnesium from neutral solutions of manganous nitrate or chloride. Phipson (*Jahresb.*, *1864*, 192) corroborates this and remarks that the manganese separates as a regulus. The observations of Roussin (*Jahresb.*, *1866*, 170), Comaille (*Comptes Rendus*, **63**, 556; *Jahresb.*, *1866*, 171), and Kern (*Chem. News*, **38**, 236), on the other hand, seem to demonstrate that metallic manganese is not thrown out of manganous salts by metallic magnesium.

We have tried the action of the last metal on manganous salt solutions, both in the presence of alcohol and ether. In using

these liquids, our aim was to reduce the liability of oxidation of manganese, if any should appear, to a minimum.

Experiment 1.—In this trial magnesium acted upon aqueous manganous chloride in the presence of alcohol for a period of two hours. At the expiration of this time the liquid was distilled off, and the material remaining was then carefully analyzed. 0.2582 gram substance was used for this purpose. It showed the presence of 0.0284 gram of chlorine, 0.1392 gram of magnesium, and 0.0539 gram of manganese, or a total of 0.2215 gram.

Experiment 2.—In this, both ether and alcohol were added to the solution upon which the magnesium acted. After removal of the liquids the residue was dried in an atmosphere of nitrogen. 0.6530 gram of it showed the presence of 0.0993 gram of chlorine, 0.3059 gram of magnesium, and 0.1865 gram of manganese, or a total of 0.5917 gram. The action of the magnesium in this instance was only continued through one and a half hours.

Experiment 3.—The conditions here were practically the same as those in experiment 2. The substance was dried, as there, in an atmosphere of nitrogen. Upon analyzing 0.7120 gram of the dry residue it revealed the presence of 0.2302 gram of chlorine, 0.2339 gram of magnesium, and 0.1779 gram of manganese.

In these three trials, as in others which were made, the sum total of the constituents of the reaction product, obtained by analysis, is less than the quantity of material taken for analysis, indicating that, in all probability, it is not metallic manganese which is precipitated by magnesium, but rather, a hydrated oxide, as was suggested by Kern, who used a saturated solution of manganous chloride, and allowed metallic magnesium to act upon it for a period of six to eight hours, with this result:

$$3MnCl_2 + 3Mg + 3H_2O = 3MnO + 3MgCl_2 + 3H_2,$$

and in the presence of water the manganous oxide passes into the protosesquioxide.

Metallic manganese thrown out by the electric current, oxidizes rapidly on momentary contact with the air, and even if it should come down as metal, through the action of magnesium, it is scarcely probable that, in the finely divided state in which it would be, it could long resist the action of the surrounding water.

UNIVERSITY OF PENNSYLVANIA,
June, 1894.

NOTE ON THE TEST FOR STRYCHNINE.[1]

By W. P. Mason and J. W. Bowman.

ORGANIC matter having been removed, and the solution containing the purified alkaloid having been evaporated to dryness on the water-bath, the dry residue is taken up with a little concentrated sulphuric acid, one of several oxidizing agents added in solid form, and the well-known strychnine color reaction forthwith appears as usual. Or, in the event of the evaporation having been accomplished in a platinum dish, such dish may be connected with the positive pole of a battery, and, upon touching the negative pole to the acid contents, the strychnine color instantly flashes out. All this being long since known, the following table is offered to indicate the relative degrees of delicacy of the several reagents commonly employed.

In each instance the figures at the top indicate the number of milligrams of strychnine sulphate actually operated upon, *i. e.*, the amount left upon the evaporating dish by the evaporation of the measured quantity of standard solution employed.

Amount used in milligrams.	0.500	0.400	0.300	0.250	0.150
$K_2Mn_2O_8$...	very strong	very strong	very strong	very strong	strong
$K_2Cr_2O_7$	very strong	very strong	very strong	very strong	strong
PbO_2	fair	fair	weak	no test	no test
$K_6Fe_2(CN)_{12}$	strong	strong	strong	strong	strong
MnO_2	strong	strong	strong	strong	strong
H_2CrO_4	very strong	very strong	very strong	strong	strong
Battery	strong	fair	no test	no test	no test

Amount used in milligrams.	0.050	0.025	0.020	0.015	0.010
$K_2Mn_2O_8$...	strong	strong	weak	very weak	no test
$K_2Cr_2O_7$	fair	weak	very weak	no test	no test
PbO_2	no test	no test	no test	no test	no test
$K_6Fe_2(CN)_{12}$	fair	fair	weak	very weak	no test
MnO_2	strong	fair	weak	weak	very weak
H_2CrO_4	weak	no test	no test	no test	no test
Battery	no test	no test	no test	no test	no test

From the foregoing it will be seen that beautiful as Letheby's galvanic test is, it does not compare favorably in point of deli-

[1] Read at the Brooklyn Meeting, August 16, 1894.

cacy with the more common ones using chemical reagents It certainly fails long before the bitter taste disappears.

From the table it would seem that MnO_2 should be given the first rank, but the slowness of its action is greatly in its disfavor, and the consequent difficulty of getting the color to flow down the side of the dish from the crystal of reagent is an objection. The presence of a little organic matter, also masks its action.

Altogether, we found that $K_2Mn_2O_8$ gave the most satisfactory results. Of course, the color of this reagent is an argument against its use, but if the acid used be of full concentration, and if a blank experiment be run at the same time with acid only in the dish, no trouble need be feared from that source.

RENSSELAER POLYTECHNIC INSTITUTE,
June 4, 1894.

THE DETERMINATION OF MELTING-POINTS AND THE COMPOSITION OF SOME CANDLE MATERIAL.

BY W. E. GARRIGUES.

Received October 15, 1894.

THE so-called melting-point of a fatty substance is obtained in such a variety of ways, and with equally varied results, that the claim of a certain figure for any particular article of commerce is really of little or no value, unless accompanied by a description of the method employed in its determination, which for ordinary trade conditions is hardly feasible.

There is probably no method in common use, even comparatively independent of personal equations and respective laboratory conditions. Those proposed for determining melting-points in capillary tubes etc., besides being open to these objections, necessitate allowing the fat to harden for many hours before applying the test. Wiley's method for butter fat is both tedious and difficult of manipulation and of course useless for free fatty acids.

The solidifying point, after Dalican, is not infrequently reported as the melting-point of stearic acid candles, and would if this were the only material employed, be an easy and fairly good solution of the problem; obviously, however, it is valueless for paraffin-wax and even for many mixtures of the two. The writer believes that any procedure which will quickly give

results on all kinds of candle material, the figures capable of being checked by different manipulators, is a much felt want among chemists engaged in such work.

In American oil refineries the melting-point of paraffin is usually determined by immersing the bulb of the thermometer to two-thirds its length in the molten wax, which is then permitted to cool slowly until the first signs of incipient solidification appear on the surface, disregarding that portion in immediate contact with the sides of the dish. The height of the mercury is then read off.

In some works this is slightly varied by drawing the point of a pin across the surface of the melted wax, until a "string" of the latter can be picked up. This is regarded as the melting-point.

A modification of Dalican's method, seemingly capable of universal application to substances solid at ordinary temperatures, was some time ago called to the writer's attention by Mr. Thomas S. Gladding. It consists of observing the temperature at which a fatty substance solidifies while in constant agitation.

The process is conducted by Mr. Gladding in the following manner: Thirty to fifty cc. of the dried sample is placed in a small beaker, the bulb of the thermometer is completely immersed therein and the glass with its contents twirled continuously in one direction until the mercury stops receding or ascending.

At first it falls rapidly and regularly but its subsequent behavior varies with the nature of the substance under examination. With fatty acids there is a rise of from 0.1° to 1° C., averaging about 0.3° for commercial stearic acid; here it remains stationary for about one minute. With paraffin-wax no rise results, but the mercury remains stationary about one-half minute and then continues to recede at the rate of 0.1° to 0.2° per minute. The fall prior to reaching this point being much swifter, no difficulty is experienced in noting the exact temperature. With mixtures of stearic acid and paraffin there is great diversity, the observed figures ranging from no rise, to one of nearly 4°. The latter representing a mixture of two-thirds stearic to one third wax.

Following is a table showing this melting-point of such mix-

tures in different proportions. The last column gives the action of the mercury at the time of solidification:

	Stearic.	Paraffin.	Melts at	
1	100	0	54.6	0.1 rise.
2	100	10	53.4	No "
3	100	20	52.4	" "
4	100	30	51.6	" "
5	100	40	50.8	0.05 "
6	100	50	50.1	0.2 "
7	100	60	49.2	0.6 "
8	100	70	48.2	0.8 "
9	100	80	47.4	2.8 "
10	100	90	45.6	0.6 "
11	100	100	45.2	0.8 "
12	90	100	45.8	No "
13	80	100	46.3	" "
14	70	100	46.9	" "
15	60	100	47.3	" "
16	50	100	47.9	" "
17	40	100	48.6	" "
18	30	100	48.9	" "
19	20	100	49.6	" "
20	10	100	50.4	" "
21	0	100	50.8	" "

To check No. 9, the same paraffin was mixed with another sample of stearic and gave:

Stearic.	Paraffin.	Melts at	
100	0	53.1	0.6 rise.
100	20	50.8	0.6 "
100	40	49.0	0.7 "
100	60	46.5	3.6 "
100	80	45.9	3.1 "

NOTE.—These tables were constructed with a view to practical uses, hence, the proportions, as above, instead of even percentages reckoned on the mixture. In candle factories the predominant material is taken as a basis of calculation. Thus, forty per cent paraffin means 100 parts stearic acid to forty parts wax.

The great advantage claimed for this method is the concordance of its results in different hands. The figures obtained are always the same to 0.1°. The only caution necessary is in cases where apparently no rise of the mercury will take place; the twirling motion should be continued until the mass assumes an unbroken white color and a homogeneous semi-solid consistency. This may take some minutes; then if still no rise occurs the temperature at which there was a pause

is to be noted. A few trials with a mixture like No. 9 will make this clear.

The thing to guard against is being deceived by an action of the mercury similar to say No. 15. For several minutes before the enormous rise in the former, it almost stops, sinking no faster than after reaching the true point in the latter. The appearance of the substance under examination is, however, vastly different, being in No. 9, coarse, white flakes floating in a clear molten liquid. On continuing the motion, the mass suddenly blends to a solid white, the temperature rising rapidly; the highest point reached being the melting-point. On paraffin-wax, the refinery test previously mentioned, shows about 0.6° C. higher than Gladding's.

Chemists have for some time been aware that a mixture of fatty acids, subjected to distillation with superheated steam, undergoes some change. It is known that a quantity of liquid hydrocarbons is formed, together with a black pitch; also that there is a slight increment in the melting-point. Alder Wright ascribes this latter to the possible formation of isoleic acid or stearolactone. A limited investigation by the writer, carried on at a large candle works, is felt to be a small grain added to a rather barren fund of literature on this subject.

An oft occurring mistake in connection with published analyses of candle material, is the omission of the details of manufacture. For instance, to give the average composition of commercial stearic acid, means absolutely nothing when we consider that one manufacturer employs palm-oil as a source while another uses tallow or bone-fat. A third both saponifies and distills with steam while a fourth uses sulphuric acid or presses the fatty acids directly without distillation. It therefore becomes essential to preface any report of this kind with a brief outline of the several stages through which the fatty substances pass.

The fats under consideration here are exclusively tallow and bone-fat. These are saponified in an autoclave under 150 pounds steam pressure and without the aid of any base. All that is of sufficiently good color is then at once subjected to pressure at ordinary temperature, followed by a second hydraulic pressing, at steam heat. The solid cake of fatty acids thus obtained,

needs only to be freed from dirt before being ready for the candle-molds. The oil expressed hot is permitted to chill, re-pressed cold, and the solid residue again subjected to the hot pressing. This is continuous, the cake from the hot press alone being used in the molding room.

The dark fatty acids, from the autoclave, before receiving the above treatment, are subjected to distillation, in copper, with superheated steam; 16,000 to 18,000 pounds constituting one "run," during which the volume in the still is kept constant by a continuous inflow from the storage tank above.

The distillate is caught in three fractions. The white oil, comprising about four-fifths of the whole is obtained first. This we will call "first run oil;" it is ready for pressing at once. The hydrocarbons that are formed having, in part at least, a higher boiling-point than the fatty acids, accumulate in the still and when these begin to come over in quantity sufficient to color the distillate a decided green, the receptacle is changed. What now comes over we will term "second run oil;" it is returned to the storage tank and redistilled with the next run.

After a time the distillate again changes color becoming darker and more viscid. The operation is then stopped and the contents of the still permitted to cool, subsequently being transferred to a smaller iron still in which a higher heat can be attained. The fraction obtained here we will designate "green oil." There now remains as a residue a black pitch, called "candle tar."

As will be seen later, from its analysis, the practice of returning this green oil to the storage tank, for redistillation with other fatty acids, can not be looked upon in any other light than as an adulteration of the red oils, finally obtained, into which it finds its way.

Going back to the autoclave we find little of interest except perhaps the degree of perfection attained by this mode of saponifying, without any base. Samples removed after ten, twelve, and fourteen hours digestion, showed respectively 1.74, 1.44, 1.06 per cent. glycerol.

NOTE.—The unsaponified fat may be approximately deduced on multiplying these figures by ten.

As might be expected, no change occurred in the constitution of the fat, other than the removal of glycerol. Facilities for trying the effect of higher pressure than 150 pounds were lacking.

Proceeding to the distillation, we find the following changes take place:

BEFORE DISTILLATION.		AFTER DISTILLATION.	
Melting-point.	Per cent. oleic acid.[1]	Melting-point.	Per cent. oleic acid.
41.5	43.96	44.5	35.06
43.6	44.64	45.5	36.06
43.9	41.67	45.0	34.00

These melting-points are lower than those of the pure fatty acids alone; due in the first column to the presence of neutral glycerides, to the extent of ten to fifteen per cent., and to hydrocarbons from a previous distillation, as before mentioned. Distillation almost eliminates the former, but the hydrocarbons are still there in about the same proportion (*vide infra*).

To determine quantitatively the changes wrought by the high temperature, about 260° C., a run of 16,075 pounds was traced through, and the chemical composition before and after noted, as well as the proportion of the different grades of oil previously named. These figures may be taken as typical, the variation from averages being very small.

The oil had a melting-point of 43.2° C. and contained:

	Before distillation, per cent.	After distillation, per cent.
Solid acids	49.52	50.47
Oleic acid	42.86	33.05
Hydrocarbons (liquid)	6.94	13.14
Glycerol[2]	1.37	
Tar		2.00
Loss		1.34
	100.69	100.00

The percentage yield of the different grades of oil and the constitution of each was:

[1] NOTE.—All the percentages of oleic acid given in this paper were obtained by calculation from the iodine absorption figure. The melting-points are those described in the beginning of this article.

[2] NOTE.—One-half the glycerol found is subtracted, together with oleic acid and hydrocarbons, from 100 to determine the solid acids, since tallow glycerides yield approximately ninety-five per cent. fatty acids and ten per cent. glycerol.

First run oil....	80.31	Containing: Hydrocarbon...	6.29	per cent.
Melting-point 44.8		Fatty acids	93.71	"
Second run oil..	12.13	Containing: Hydrocarbon...	35.90	"
		Fatty acids	64.10	"
Green oil.....	4.22	Containing: Hydrocarbon...	98.74	"
Tar.....	2.00	Fatty acids	1.26	"
Loss.....	1.34			
	100.00			

Making corrections for the hydrocarbons present before distillation and the glycerol, which forms a large part of the 1.34 per cent. loss, we have as a result of distilling 100 parts of pure fatty acids:

	Before.	After.
Solid acids.....	53.61	54.63
Oleic acid.....	46.39	35.77
Hydrocarbons (liquid).....		6.71
Tar.....		2.15
Loss.....		0.74
	100.00	100.00

It seems reasonably assured, from these figures, that the stearic and palmitic acids distill without change, while the oleic partly splits up into liquid hydrocarbons, tar, and a saturated or non-iodine consuming fatty acid. The nature of this body, though it has not been isolated, will be considered briefly farther on.

From the foregoing facts, it appears to the writer that the present process of manufacture might be advantageously altered by taking the fatty acids directly from the autoclave to the presses—as is done with the light colored stock—and obtaining a press-cake melting at 55°–56°, which latter is then subjected to distillation. By these means the candle stock would not deteriorate in the still as it now does (*vide infra*), and the formation of valueless—and even for most purposes harmful—hydrocarbons would be avoided, giving the red oils a greater worth.

Practical candle makers find that distilled stock invariably yields a press-cake of lower melting-point than that from the autoclave. This is now explained by the formation of the saturated fatty acid from oleic acid, in the still. This body is sufficiently solid to resist being pressed out with the oleic acid, yet

soft enough to lower the melting-point of its associates—stearic and palmitic.

NOTE.—As shown by several writers, the lowering of the melting-point of a mixture of two fatty acids by the addition of a third, does not necessitate the latter having a melting-point below that of the two former.

Apart from the evidence already given its presence is indicated by its low molecular weight, being—probably considerably—under 268, while the mean of stearic and palmitic as occurring in tallow is 271–272. The following tabulated analyses of press-cakes in different stages of completion, illustrate these points.

	AUTOCLAVE STOCK.				STILL STOCK.		
	Melting-point, ° C.	Per cent. oleic acid.	Total mean equivalent.	Molecular weight of solid acids.	Per cent. oleic acid.	Total mean equivalent.	Molecular weight of solid acids.
1....	51.0				16.69		
2....	51.5	21.08					
3....	53.6				7.02		
4....	53.8	11.57					
5....	54.1	9.00					
6....	54.3				6.51	269.2	268.3
7....	54.4	8.40			5.51	269.2	268.4
8....	54.5				5.96	268.4	267.5
9....	54.6				6.00	268.0	267.0
10....	54.8				4.99	268.4	267.6
11....	54.9	6.60	272.0	271.2	4.16	270.0	268.4
12....	55.5	4.37					
13....	55.6	4.02	272.0	271.5			
14....	56.0	3.74	272.8	272.4			
15....	56.1	3.96	272.0	271.5			
16....	56.2	3.03					...

NOTE.—The average content of neutral glycerides was determined to be 3.90 per cent. in samples 11, 13, 14, 15, from the autoclave, which is offset by an average of 0.17 per cent. hydrocarbons in samples 6 to 11, inclusive, from the still. In calculating the mean equivalents, no corrections were made for these in either case. The method of determination was; boiling with an excess of alcoholic potash and back titrating.

To sum up, in conclusion, it appears that when oleic acid is distilled in an atmosphere of steam, the distillate contains, besides unaltered oleic acid, hydrocarbons—liquid, and mainly of high boiling-point—and one or more fatty acids, not isomerides of oleic, having a considerably higher melting-point and lower mean equivalent than the latter, and differing therefrom in not forming addition products with iodine. A black pitch remains as a residue in the still.

SOME RECENT CONTRIBUTIONS TO OUR KNOWLEDGE OF METALLIC REDUCING AGENTS.[1]

By H. F. Keller.

IN the extraction of metals from their oxygen compounds, carbon is certainly the most important and useful reducing agent. Its great affinity for oxygen is utilized in the manufacture of iron and steel; the commercial production of other useful metals, such as copper, lead, zinc, and tin is accomplished, either directly or indirectly, with its aid; and under its influence even the energetic metals of the alkalies release their powerful grip upon oxygen. Contrasted with this, the use of other substances for the purpose of abstracting oxygen is almost insignificant. Is it surprising, therefore, that carbon is looked upon as the reducing agent *par excellence*, or that the very idea of reduction seems to us inseparably associated with this element?

But the reducing power of a substance depends, in a large measure, upon temperature. It is well known to chemists that, under certain conditions, many metals have affinities which are far more powerful than those of carbon. When we glance over the pages of our chemical text-books, we see described there numerous experiments based upon the superior combining power of iron, aluminum, zinc, magnesium, and the alkali metals. The great Swedish chemist who arranged the elements according to their supposed affinities in an electro-chemical series, was among the first to employ the positive alkali metals for isolating and preparing other elements. His method consisted in decomposing the halogen compounds by means of potassium; and it was subsequently improved by Berzelius' distinguished disciple, Wöhler. With its aid, the latter chemist not only succeeded in reducing for the first time those remarkable metals, aluminum and glucinum, but he also showed that *all* those metals, the oxides of which cannot be reduced by either carbon or hydrogen, may be obtained by the action of potassium upon their halogen compounds.

It must not be supposed, however, that the use of metals as reducing agents is confined to the laboratory and the lecture

[1] First published in the Journal of the Franklin Institute, October, 1894.

table. Practical applications of such reactions may be less conspicuous, but they constitute, nevertheless, the basis of not a few important metallurgical processes. The "precipitation" of lead from its sulphide ores; the solution of silver by the nascent lead in the blast-furnace; the amalgamation of the same metal in the iron pan; Deville's process of extracting "silver out of clay," recently so greatly perfected by Castner and Netto—are they not essentially reductions by means of metals?

In view of the facts mentioned, it may appear strange that comparatively little progress was made for many years in the study of the reducing properties of metals. We can, however, satisfactorily account for this when we consider the great tendency of metals to form alloys; it is difficult, in many cases indeed impossible, to obtain products entirely free from the reducing metal, and it is also well known that even a trifling amount of such an impurity may seriously impair the valuable qualities of a metal. Another obstacle has been the high price of those metals, which, by reason of their more powerful affinities, could, with advantage, be substituted for carbon.

Recent improvements in the commercial production of some of these metals have partially removed the latter obstacle. Thanks to the rapid progress of electro-metallurgy, aluminum is now to be had for about half a dollar per pound; sodium, once a chemical curiosity, is manufactured on an enormous scale at a less cost even than aluminum; and magnesium, now successfully extracted from carnallite, is applied to a variety of technical uses.

The radical changes which have taken place in our views on chemical affinity, as a result of the study of thermo-chemical phenomena, and the theory that the properties of the elements are *periodic functions* of their atomic weights, have also largely contributed to awaken interest and activity in the subject of our discussion.

The remarkably high heats of formation of its oxide and chloride, as well as the great stability of these compounds, render the action of magnesium upon other oxides and chlorides particularly interesting. Clemens Winkler, of Freiberg, has presented us with a most careful and systematic investigation of

the reducing action of this metal upon oxides, while Seubert and Schmidt have communicated a similar exhaustive study of its action upon chlorides.

In giving a brief résumé of the results obtained by these experimenters, I shall adhere to the order adopted by them. It is based upon the periodic system, and has the advantage of showing many interesting relations that might otherwise escape notice.

GROUP I.

Group I embraces a main group consisting of lithium, sodium, potassium, rubidium, and cesium, and a sub-group consisting of copper, silver, and gold.

Owing to the difficulty of obtaining the oxides of the alkali metals in a pure condition, the carbonates were employed. It was found that to insure the best results three atoms of magnesium are required for every molecule of the carbonate, thus: $Na_2CO_3 + 3Mg = 3MgO + C + 2Na$.

The carbon as well as the sodium are deprived of their oxygen. It was found that, with the exception of cesium carbonate, the alkaline carbonates *suffer reduction* to the metallic state when heated with magnesium, but that the intensity of the reaction diminishes as the atomic weight of the metal increases. Lithium, *e. g.*, whose atomic weight is only seven, was reduced with explosive violence, the metal being completely vaporized, while the tube in which the reduction was effected was shattered to pieces; potassium (atomic weight 39), and rubidium (atomic weight 85) on the other hand, were reduced quickly and without notable vaporization.

The reduction may be made in a tube of hard glass closed at one end; it is better observed, however, by conducting it in a current of hydrogen.

The preparation of potassium affords a most instructive experiment, which may well serve for lecture demonstration.

Into a wide tube of Bohemian glass, a porcelain boat, containing about two grams of the mixture of potassium carbonate, and magnesium is introduced. A current of perfectly dry hydrogen gas is passed through the tube, and the part of the tube surrounding the boat is gradually heated to incipient redness;

the mass darkens, and upon further raising the temperature with the aid of the blast-lamp, the reduced potassium is completely expelled from the boat, exhibiting the deep green color of its vapor, and is deposited in the form of a bright mirror in the cooler part of the tube. At the same time the hydrogen flame shows an intense violet color. The dark residue remaining in the boat consists of magnesia and carbon. Enough potassium will have collected to show its color, luster; that it is sectile, fusible; its action upon water, bromine, etc.

In view of the high price of metallic potassium, the question as to whether the described reaction might not be carried out on the large scale suggested itself. Experiments showed, however, that in the absence of a gas current, the distillation of the metal is very incomplete; and inasmuch as carbon monoxide forms an explosive compound with this metal, illuminating gas could not be substituted; in fact, the explosive carbonyl-potassium was invariably formed when the quantity of magnesium present was insufficient for the *complete* reduction of the carbonate.

This was further proved by experiment. When two atoms only of magnesium were taken, the reaction took place according to the equation:

$$CO\begin{matrix}OK\\OK\end{matrix} + 2Mg = CO + 2K + 2MgO.$$

More promising results were obtained by employing potassium hydroxide instead of potassium carbonate. The danger of forming the explosive body is thus avoided, while the hydrogen gas set free simultaneously with the potassium, insures the complete distillation of the latter:

$$KOH + Mg = K + H + MgO.$$

The reaction is somewhat violent, but may be moderated by adding some inert substance, such as magnesia, or by using the magnesium in the form of lumps or bars.

Winkler says "it does not seem unlikely that the manufacture of potassium could be carried out by means of the same apparatus, and the same operations, which C. Netto has so successfully employed in reducing caustic soda with carbon. Into a retort filled with bars of magnesium, and heated to redness, melted potash would be allowed to flow in a continuous stream, while

the escaping mixture of potassium vapor and hydrogen is being cooled."

Winkler figures the cost of a pound of potassium to be about $3.75; the metal is now quoted at $28.

Beketow, who had previously made use of the action of aluminum upon potassium hydroxide, obtained only one-half of the theoretical yield owing to the simultaneous formation of potassium aluminate.

The sub-group, consisting of the heavy metals copper, silver, and gold, exhibited the reverse behavior; the reduction was more energetic the higher the atomic weight of the metal. A very *slight* deflagration accompanied the removal of oxygen from cuprous oxide, while silver oxide was reduced with *explosive violence*. Very curiously aurous oxide was not visibly affected by the magnesium. This is explained, however, by the fact that gold oxide splits up into its constituents considerably below the ignition point of magnesium.

GROUP II.

The main group comprises glucinum, magnesium, calcium, strontium, and barium; and zinc, cadmium, and mercury, constitute the sub-group.

These elements are bivalent, and the action of their oxides upon magnesium is therefore:

$$R''O + Mg = MgO + R''$$

In some cases the *hydroxides* were also used.

Glucina was easily reduced by magnesium; the mass became slightly incandescent, but some unaltered oxide was found in the residue.

There was no action observed when a mixture of magnesium and magnesia was heated in hydrogen; the oxide remained in the boat, while the metal sublimed in beautiful crystals. The existence of Beetz's suboxide could not be confirmed.

No visible sign of chemical action occurred when lime and magnesium were heated together. The reduction proved nevertheless to be almost complete.

A slight incandescence attended the reduction of strontia, whilst barium oxide displayed an energetic action upon magnesium. In both cases the decomposition was apparently complete.

None of the alkaline earth metals were found to be volatile at the temperature of reduction.

The hydroxides were even more readily acted upon than the oxides; so striking and beautiful, indeed, were the phenomena observed in the cases of calcium hydroxide and strontium hydroxide, that Winkler proposes to utilize them for lecture illustration, and in pyrotechnics.

The reduction of the oxides belonging to the sub-group was very energetic, the resulting metals being vaporized completely. Cadmium oxide develops less energy than either zinc oxide or magnesium oxide.

Both in the main group and the sub-group, the maximum of chemical energy occurs in the second member.

GROUP III.

The main group embraces boron, aluminum, (scandium,) yttrium, lanthanum, and ytterbium, and gallium, indium, and thallium, form the sub-group. Three atoms of magnesium are required to abstract the oxygen from their oxides:

$$R_2O_3 + 3Mg = 3MgO + 2K'''$$

Phipson has observed that boric acid is reduced upon ignition with magnesium. With the aid of magnesium, boron was also obtained by Geuther from the boro-sodium fluoride, and quite recently L. Gattermann has shown that boric acid, as well as borax can be reduced by means of this metal, so as to yield products which are suitable for the preparation of various volatile boron compounds.

Winkler confirmed these observations. He states that the trioxide and the borate of sodium are easily reduced, the latter with much energy and evolution of sodium vapor. But he found that, instead of free boron, the residue contains magnesium boride of variable composition; for, on treatment with hydrochloric acid, boron hydride is given off as a gas. Sometimes a solid residue remains, which is likewise a compound of boron and hydrogen.

Owing to the acid-forming character of boron, the reduction was never complete; borates, upon which magnesium has no action, are always formed.

An attempt was also made to prepare a boron suboxide by limiting the supply of magnesium, thus:

$$B_2O_3 + Mg = 2BO + MgO$$

but no indication of such an oxide was observed.

A dark colored product resulted from heating alumina with magnesium. The reaction appeared to be quite energetic; the mass exhibited a vivid glow and increased largely in volume. In addition to finely divided aluminum, a new oxide, AlO, and magnesium spinel had been formed. This monoxide could not be obtained in a pure condition, but its existence was proved beyond doubt. It is best prepared by heating in a current of hydrogen, a mixture corresponding to

$$Al_2O_3 + Mg = 2AlO + MgO.$$

This oxide is a brownish-black, voluminous powder, is pyrophoric, and liberates hydrogen slowly from water; it precipitates cuprous oxide from copper sulphate solution, and is exceedingly susceptible to oxidation.

Winkler suggests that the blue color of sapphire, and possibly also that of ultramarine, may be due to a small proportion of this monoxide.

Of the rare earths of group III, only yttria and lanthana were subjected to the action of magnesium. The energy of the reduction appeared to increase with the atomic weights.

Upon the oxides of the sub-group, magnesium reacts with great violence; the intensity of reduction has its maximum in In_2O_3.

The behavior of Tl_2O_3 towards magnesium, appears to be an exception. Before the temperature of reduction is reached, this oxide splits up into Tl_2O and O_2, and the thallous oxide so formed is then only partially reduced. Thallium carbonate, however, is deprived of its oxygen completely and with explosive violence.

GROUP IV.

The most interesting results, perhaps, were obtained in the fourth natural group of elements.

The known properties of carbon, silicon, titanium, zirconium, cerium, and thorium, assign them positions in the main group, while germanium, tin, and lead, constitute the sub-group.

In addition to their acid-forming dioxides, the majority of these elements are capable of giving monoxides. It was therefore deemed desirable to attempt not only the complete reduction of the higher oxides, but also a *partial* removal of the oxygen with a view to procure the lower oxides.

The statements of different experimenters concerning the action of carbon dioxide upon magnesium are somewhat conflicting.

That a ribbon of the metal will burn in an atmosphere of carbon dioxide was first observed by Kessler, but neither he nor other chemists who repeated and modified his experiment explained satisfactorily the nature of the reaction.

Winkler shows, in the first place, that magnesium, when *moderately* heated in a current of carbon dioxide, does not take fire, but is slowly converted at its surface into a carbide, carbon monoxide being formed at the same time. Upon increasing the heat to a full redness, the metal was inflamed and continued to burn with a dazzling light. The products of this combustion are magnesia and carbon.

When the magnesium is employed in the form of powder, these reactions take place even more readily. At a temperature considerably below a red heat carbon monoxide appears, and its quantity is greatly increased when low redness is reached. The metal burns with great brilliancy at a full red heat, and unless the current of carbon dioxide is very rapid, its reduction is complete.

It has already been mentioned that a separation of carbon was observed when magnesium acted upon carbonates; also that carbon monoxide was formed when an excess of the carbonate was present. Further experiments were made with calcium carbonate. A mixture of this substance with magnesium: $CaCO_3 + 3Mg = Ca + C + 3MgO$, heated in a current of hydrogen detonated violently. The examination of the débris, revealed the presence of a carbide of magnesium. No metallic calcium was observed in the residue when only two atoms of magnesium were used for each molecule of the carbonate.

According to Kessler, burning magnesium is extinguished in carbon monoxide, while Parkinson asserts that at a red heat the

metal burns vividly in this gas. Both observations were found to be correct. A spiral of magnesium wire ignited in the air, ceased to burn while introduced into a jar of carbon monoxide, but when strongly heated in a current of the gas the magnesium emitted light, and a gray coating of a carbide appeared on its surface.

Numerous experiments to determine the exact composition of this carbide were made, but without yielding a definite result.

Silicon exhibits a pronounced tendency to combine with magnesium. Silicon-magnesium was first observed by Wöhler, in 1858.

The reduction of silica by metallic magnesium was observed in 1864, by Phipson, and Parkinson showed in 1867 that silicon-magnesium, as well as a magnesium silicate, are formed at the same time. A few years ago L. Gattermann published an interesting paper, in which he showed how very easily silicon dioxide is reduced by magnesium. He states that either silicon or silicon-magnesium can be obtained by varying the proportion of magnesium; and he applies the reaction to the preparation of volatile compounds of silicon, such as the chloride, bromide, iodide, silicoformic acid, silico-chloroform, etc.

Gattermann and Winkler agree that an energetic reaction occurs upon heating a mixture of one molecule of silica and two atoms of magnesium.

$$SiO_2 + 2Mg = Si + 2MgO.$$

By adding magnesia to the mixture, the heat of the reaction was moderated, but it was then found that much silicon-magnesium was contained in the product. If the reaction be effected at low temperature and in the presence of an excess of magnesium, silicon-magnesium is always formed, while at a high heat or in presence of magnesium, only amorphous silicon results.

A silicon monoxide could not be obtained by the reduction of silica, either by magnesium or silicon.

Many silicates are reduced quite as easily as the dioxide; in some cases the metallic base is likewise reduced, *e. g.*, potash glass.

None of the oxides studied presented greater difficulties than

titanium dioxide. The results may thus be summed up: Titanium dioxide was not reduced to the metallic state; a mixture of monoxide and a titanium spinel were the products of the reaction. Other intermediate oxides were sometimes formed. When the residue was treated with hydrochloric acid, HTi_3O_4 was formed, which, upon heating, gave TiO_2 and hydrogen. Neither titanium-magnesium, nor a titanium hydride, was observed.

The reduction of zirconia was effected by heating it with magnesium to a high temperature. A monoxide could not be identified with certainty; and $ZrMg_2$ does not appear capable of existing.

According to the amount of magnesium employed either cerium or Ce_2O_3 were obtained from cerium dioxide. An intermediate monoxide was not formed. The reduction begins at a moderate red heat and is accompanied by a vivid glow. A considerable proportion of the magnesium is volatilized. In the nascent state, cerium was found to absorb hydrogen in large quantities.

The formation of a metallic hydride at a bright red heat is a most remarkable observation. It is clearly proved to be correct by the following experiment.

A mixture is prepared according to the equation:

$$CeO_2 + 2Mg = Ce + 2MgO$$

Twenty grams of this mixture are placed in a combustion tube through which a current of dry hydrogen is passed, while a gentle heat is applied to expel any moisture. The further end of the tube is then closed with a strong clip. Hydrogen is allowed to enter the other end and the heat quickly raised to bright redness; a rapid current of hydrogen is seen to pass through the wash-bottles into the tube.

The hydride is of a brownish-red color. It is without action on water at ordinary temperatures, but sets free hydrogen upon heating. Hydrochloric acid dissolves it to $CeCl_3$, with evolution of hydrogen. It was found impossible to completely remove magnesia from the product. The hydride is very inflammable, and detonates with potassium chlorate, potassium nitrate, etc.

The analytical results obtained point to the formula CeH_2.

After the existence of a cerium hydride had thus been established, the thought suggested itself that the other elements of Group IV might possibly be capable of forming similar compounds. Only carbon and silicon were known to form hydrides, but these elements could not be made to unite with hydrogen when their oxides were reduced by magnesium. Since titanium could not be reduced to the metal, it is not strange that all efforts to form a hydride gave negative results; zirconium and thorium did absorb hydrogen and yielded hydrides similar to CeH_2. The same was observed with lanthanum and this led Winkler to believe that this element belongs to the cerium group; but he showed subsequently that yttrium and other trivalent elements, and even the divalent barium, strontium, and calcium can unite with hydrogen.

These hydrides represent a new class of metallic compounds, in which only half the usual valence of the metals is satisfied.

The action of magnesium upon chlorides has been made the subject of an elaborate research by Seubert and Schmidt.

I must content myself with a very brief statement of some of the main results obtained by these chemists.

Both the anhydrous bodies and the aqueous solutions of the chlorides were subjected to the action of magnesium.

In the former case the substance, either mixed with magnesium powder, or conducted over it in the form of vapor, was heated to a high temperature. It was found that all chlorides could thus be reduced to the metallic state, but the reduction was incomplete in the groups of the metals of the alkalies and the metals of the alkaline earths.

In *neutral* aqueous solutions, all the metallic chlorides, save those of the alkalies and those of the alkaline earths, gave up their chlorine to the magnesium. In some cases the metals were deposited in the metallic state, (silver, gold, thallium, lead, arsenic, antimony), but in most cases, hydroxides were precipitated. These hydroxides always represent the lowest state of oxidation. $CuCl_2$, *e.g.*, is changed into Cu_2O; chromium, aluminum, iron, manganese, cobalt and nickel, all yielded hydroxides.

It would seem that the tendency to form such hydroxides is

peculiar to the positive metals, and especially to those forming basic salts. Seubert and Schmidt believed this to be due to a dissociation of the chlorides into hydroxides and hydrochloric acid. They suppose, for instance, that an aqueous solution of $AlCl_3$, contains $Al(OH)_3$, $3HCl$. This view is rendered quite probable by the fact that solutions of copper, nickel, cobalt, and chromium exhibit the color of their *hydrated* salts.

Of other metals whose oxides possess a high heat of formation, aluminum has found some application in the reduction of oxides. Beketow has employed it with success to prepare some of the metals of the alkalies; and the experiments of Greene and Wahl of reducing manganese oxides by means of metallic aluminum are still fresh in our memory.

I am convinced that a continued study of the relative affinities of the metals for oxygen and other negative elements, will lead to important applications in metallurgy, and give new and valuable methods to synthetic and analytical chemistry.

OBSERVATIONS ON AMERICAN OIL OF TURPENTINE.

By J. H. Long.

Received October 24, 1894.

IN the February, 1893, number of the *Journal of Analytical and Applied Chemistry* I called attention to certain peculiarities of our American turpentine-oil as distilled from the crude turpentine produced in the southern states.

It is well known that the chief difference between the so-called French and American turpentines is found in their behavior toward polarized light, the French oil being laevo-rotatory, while that produced here has always been described as dextro-rotatory.

In the course of the examination of a large number of samples distilled in the laboratory from fresh crude turpentine sent me directly, I found that some disclosed a very low rotation, and a few were even laevo-rotatory. Through the courtesy of Mr. E. B. Martin, of Louisville, I was supplied with crude "gum" collected in small amounts from single trees, and from the tests of these samples it appeared that the laevo-rotation was

found only in the product from the so-called spruce trees, sparingly represented in the lower turpentine-producing region. As this spruce pine (*P. glabra*) is not considered important from the standpoint of the industry I found difficulty in securing material enough for satisfactory investigation. However, in April of this year six samples of the dip, or crude liquid exudation, collected near Mobile, from as many different trees, were sent me and from these I distilled the oils used in the tests below.

In odor, color, specific gravity, and boiling-point these oils showed no unusual features, the average specific gravity at $\frac{20°}{4°}$ being 0.862. When examined by the polarimeter, using the 200 mm. tube, I found the "observed angle of rotation," α, as follows:

No. 1	$\alpha_D =$	$-64.750°$
" 2	"	$-69.075°$
" 3	"	$-64.541°$
" 4	"	$-63.100°$
" 5	"	$-63.333°$
" 6	"	$-70.333°$

The laevo-rotation is in all cases very marked, the specific rotation in the last amounting to

$$[\alpha]_D = \ldots\ldots\ldots -40.79°$$

It is also interesting to note that the results are close for the six samples, but as the trees yielding them grew in the same orchard, and, therefore, under practically the same conditions, and as the samples were taken at nearly the same time, this agreement should not be unexpected. It may be recalled that the laevo-rotation of the French oil has usually been found much more uniform than the rotation of the American oil.

These observations seem to show the probable correctness of my former suggestion; *viz.*, that the negative rotation sometimes found in American oil may be due to the presence of products from spruce trees. This appears all the more probable when it is remembered that in numerous oils examined, known to be free from spruce, a marked positive rotation was always noted, while a low positive rotation was found only in those oils distilled in parts of the country where the spruce is occasionally found.

In the further study of these oils I mixed distillates 1 and 3 above and redistilled fractionally. The fractions were polarized as before with the following results:

Temperature.			α_D in 200 mm. tube.
156.	to	156.7	—69.133°
156.7	"	157.2	—67.683°
157.2	"	157.6	—65.930°
157.6	"	159.4	—63.200°
159.4	"	162.7	—57.883°

A mixture of 2 and 6 gave:

Temperature.			α_D in 200 mm. tube.
156.	to	156.2	—73.350°
156.2	"	156.7	—72.416°
156.7	"	157.2	—71.066°
157.2	"	158.7	—68.865°
158.7	"	162.7	—65.160°

These results confirm those obtained from other oils, showing that the absolute amount of rotation is decreased in the higher fractions.

It was stated by Berthelot (J. B., *1853*, p. 522) that the dextro-rotatory American oil when heated in sealed tubes to above 250° is transformed into a substance with higher boiling-point and negative rotation. To test this behavior in the present case I heated a portion of the first fraction from 1 and 2 to a temperature of 280° during two hours in a sealed glass-tube. On cooling it was polarized without redistillation, and showed in the 200 mm. tube

$$\alpha_D = \ldots\ldots\ldots\ -15.33°.$$

The product was then sealed and heated again to 300° through several hours. On cooling, it was found to be yellowish and somewhat viscid; on distillation the liquid was found to have a much higher boiling-point than the original turpentine, but little passing over below 170°.

Three-fourths of the product distilled between this point and 250°, and this portion polarized gave in the same tube

$$\alpha_D = \ldots\ldots\ldots\ -19.560°.$$

A fraction of the distilled liquid collected from 175°–180° was strongly laevo-rotatory also.

The residue was very dark and became thick and resinous on

exposure to air. The distilled liquid had a marked odor of oil of lemons and this with its rotation suggest that it must be identical with the product described by Berthelot as iso-terebenthene, which may be obtained also from the laevo-rotatory French oil. While the ordinary product of long heating of turpentine-oil seems to be inactive dipentene we have here a very stable active product which is probably mainly laevo-limonene.

CHICAGO, October 22, 1894.

IRIDIN, THE GLUCOSIDE OF THE IRIS ROOT.

BY G. DE LAIRE AND FERD. TIEMANN.
[TRANSLATED AND ABRIDGED BY S. S. EMERY.]

(*Continued from Page 411 of Volume XV.*)

Iretol.—Iretol, the third decomposition product of irigenin, may be separated from the alkaline solution of the three by supersaturating with dilute sulphuric acid (1 : 2), neutralizing with potassium carbonate, and, after filtering from the separated potassium sulphate, shaking ten to twelve times with ether, which dissolves only the iretol. The ether can not be completely distilled from this extract, as the crude iretol forms condensation products which are insoluble in water and ether; hence the last portion of the ether must be allowed to evaporate in the air. The iretol thus obtained is a crystalline mass, easily soluble in water, alcohol, ether, and acetic ether. By fractional precipitation by chloroform from the acetic ether solution it is obtained as white needles, melting at 186°.

Its molecular weight was found to be:

1. By the lowering of the freezing-point of a glacial acetic acid solution. (Raoult's method.)	2. By the raising of the boiling-point of an alcoholic solution.	Calculated for $C_7H_8O_4$.
181.2	159	156

It contains one methoxyl group, as shown by the following determinations:

ANALYSIS.

	Per cent. (OCH_3).
Calculated for $C_6H_5O_3(OCH_3)$	19.87
Found	17.26—19.22

Tribenzoyliretol, $C_7H_9O_4(CO.C_6H_5)_3$. — Tribenzoyliretol is obtained by treating an absolute alcohol solution of one molecule of iretol and three molecules of sodium ethylate with a slight excess of benzoyl chloride and letting stand several days in the cold. It is separated by removing the alcohol by steam, extracting with ether, and, after shaking with dilute soda solution, evaporating, when it is obtained as an oily substance, which solidifies after several weeks to a transparent resin, easily soluble in alcohol, ether, acetic ether, benzene and chloroform, but insoluble in water and ligroin.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{28}H_{20}O_7$	71.79	4.27
Found	71.03	4.68

From the foregoing, it is evident that iretol contains one methoxyl and three hydroxyl groups, and that its empirical formula is $C_6H_3(OCH_3)(OH)_3$, according to which iretol appears to be the monomethyl ether of a tetroxybenzene. The correctness of this view is established by the conversion of iretol into phloroglucinol.

This is accomplished by treating the cold dilute (1 : 10) aqueous solution with sodium amalgam, and, after destroying the excess of amalgam by heating on the water-bath, adding a slight excess of sulphuric acid and then distilling. The distillate consists of very dilute methyl alcohol with traces of acetone. The ether extraction of the residue, on evaporating, gave pure phloroglucinol, melting at 208°, its identity being established by the following:

ANALYSIS.

	Per cent. water of crystallization.	
Calculated for $C_6H_6O_3.2H_2O$	22.22	
Found	22.38, 22.92	

	Per cent. C.	Per cent. H.	
Calculated for $C_6H_6O_3$	56.98	4.76	In the anhydrous
Found	59.94, 56.71	4.64, 4.70	phloroglucinol.

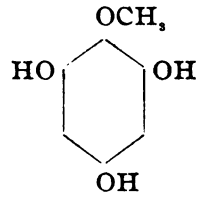
	Molecular weight.
Calculated	126
Found (raising of boiling-point of alcoholic solution)	121

The triacetyl derivative formed from the phloroglucinol melted at 106° (104°–106° according to Hlasiwetz[1] and Herzig[2]). Finally, we prepared tribenzoylphloroglucinol $C_6H_3(OCOC_6H_5)_3$, crystallizing from alcohol and melting at 172°.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{27}H_{18}O_6$	73.97	4 11
Found	73.40	4.10

The phloroglucinol is formed from the iretol according to the equation $C_7H_8O_4 + 2H = C_6H_6O_3 + CH_3OH$, from which it is evident that iretol is a methoxyphloroglucinol, having the constitutional formula



Properties and Reactions of Iretol:—Melts at 186°; easily soluble in water.

(*a*) *In Aqueous Solution.*—Violet color, changing to brownish red, with ferric chloride.

Red precipitate of benzeneazoiretol with anilin nitrate, sodium nitrite, and a few drops of strong acid.

(*b*) *In Alcoholic Solution.*—A white, crystalline condensation product with a solution of benzaldehyde in six times its volume of concentrated hydrochloric acid. Substitution of vanallin for benzaldehyde gives violet-colored solution before precipitation.

The last three tests are characteristic, although also given by resorcinol and phloroglucinol.

(*c*) *With Bromine.*—In ethereal solution, gives bromine substitution products.

In ethereal solution in the presence of water gives hexabromacetone, $Br_3C.CO.CBr_3$.

[1] *Liebig's Annalen*, 119, 201.

[2] *Wiener Monatshefte für Chemie*, 6, 888.

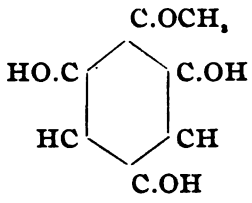
Bromine in caustic alkali, instead of free, gives bromoform, the hexabromacetone first formed being readily decomposed by the alkali into carbon dioxide and bromoform.

Sodium nitrite, with acetic acid in slight excess, converts it into the sodium salt of dinitrosoiretol, $C_7H_8NaN_2O_6.2H_2O$, separating in red crystals.

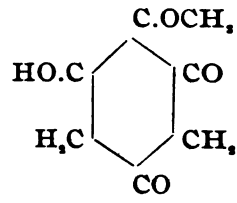
Tetroxybenzene 1.2.3.5.—The methyl in the methoxyl group of iretol can be easily replaced by hydrogen, by heating with dilute hydrochloric acid in a closed tube. Monochlormethane is given off. After removing the hydrochloric acid with lead and silver carbonate, and the water by evaporation in a partial vacuum, the tetroxybenzene was obtained as an amorphous substance, soluble in water, alcohol, ether, acetic ether, but insoluble in benzene, chloroform, and ligroin.

Isomerism of Iretol.—The properties and reactions of iretol, and also the difficulty in obtaining pure the corresponding tetroxybenzene, are explained by its isomerism, its two forms being

I.



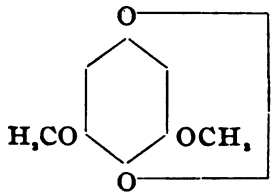
II.

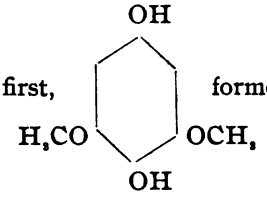


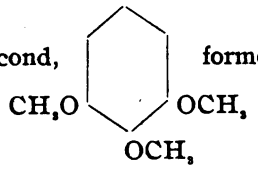
Form II undergoes hydrolysis on treating with alkali, acetone, and acetic acid being found.

This isomerism is substantiated by the following:

Methyl Derivatives of Iretol.—Tetroxybenzene yields a di- and tetra-methyl ether, prepared from the dimethoxyquinol

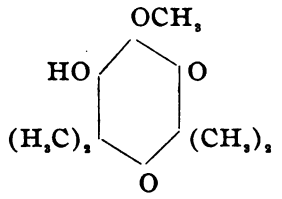


the first,  formed by reduction of the quinol, and the

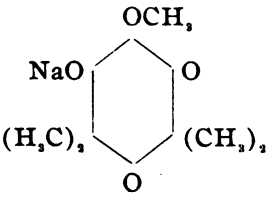
second,  formed by methylating the dimethyl product.

We have not succeeded in preparing this last from iretol.

Tetramethyliretol



is prepared by treating the methyl alcohol solution of iretol (five grams) in an atmosphere of hydrogen, with sodium (three grams) dissolved in methyl alcohol, and with iodomethane (twenty grams). The methylation is induced by shaking the flask, and is accompanied by a rise of temperature. The sodium salt of tetramethyliretol is separated by evaporating and precipitating with concentrated caustic soda. The yield is about one-third of the theoretical, the remainder of the iretol being converted into oily methyl derivatives. The salt crystallizes in long white needles, with three molecules of water, and suffers efflorescence, at ordinary temperatures, in a partial vacuum. Its constitutional formula is



ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. Na.	Per cent. H_2O.	Per cent. OCH_3.
Calculated for $C_{11}H_{15}NaO_4.3H_2O$ ($=C_{11}H_{21}NaO_7$)..	45.83	7.29	7.98	18.75	10.76
Found	45.57, 45.50	6.94, 6.99	7.76, 7.75	18.82, 18.20	10.74
In the anhydrous salt:					
Calculated for $C_{11}H_{15}NaO_4$	56.41	6.41	9.83		
Found.....	56.55, 56.04	7.17, 7.18	9.70		

Sulphuric acid liberates free tetramethyliretol, insoluble in ligroin, but soluble in hot water, alcohol, ether, acetic ether, benzene, and chloroform. It crystallizes in glistening white needles, with one molecule of water, melting at 97°; effloresces in a partial vacuum, the anhydrous substance melting at 104°.

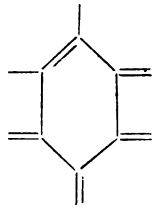
ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. H_2O.
Calculated for $C_{11}H_{16}O_4.H_2O$,($=C_{11}H_{18}O_5$).....	57.39	7.83	7.83
Found	56.98	7.86	8.06
In the anhydrous substance:			
Calculated for $C_{11}H_{16}O_4$.....	62.27	7.55	
Found	62.41	7.51	

Benzoyltetramethyliretol, $C_{11}H_{15}(COC_6H_5)O_4$, formed by the action of benzoylchloride on the sodium salt of tetramethyliretol in alcoholic solution, crystallizes therefrom in white tablets, melting at 84°.

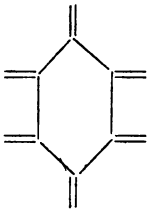
From the constitutional formula of tetramethyliretol (page 851), it is evident that by oxidation it breaks up into dimethylmalonic acid, isobutyric acid, and formic acid. By fusion with caustic potash, these products were actually obtained.

Dihydrotetramethyliretol.—Tetramethyliretol is a derivative of tetrahydrobenzene.



On treating with sodium amalgam, at ordinary temperature,

it takes up two atoms of hydrogen, apparently passing into the hexahydrobenzene form

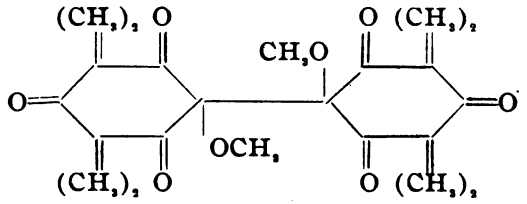


and this view is substantiated by the conversion of iretol into phloroglucinol. After destroying the excess of amalgam by heating on a water-bath, the sodium salt of dihydrotetramethyliretol may be crystallized out, or the free dihydrotetramethyliretol may be obtained by acidifying before crystallizing, when it forms transparent, rhombohedral crystals, containing one molecule of water, which is slowly given off on standing in a partial vacuum. The crystallized substance melts at 107°, the anhydrous at 139°. It is easily soluble in water, alcohol, ether and chloroform, and is precipitated from the latter by ligroin. It is not attacked by bromine nor permanganate, and, in general, does not differ widely from the tetramethyliretol.

ANALYSIS.

	Per cent. C.	Per cent. H.
Calculated for $C_{11}H_{18}O_4.H_2O$	56.90	8.62
Found	56.90	8.67
In the anhydrous substance:		
Calculated for $C_{11}H_{18}O_4$	61.68	8.41
Found	61.71	8.72

Dehydroditetramethyliretol, $C_{22}H_{30}O_6$.—



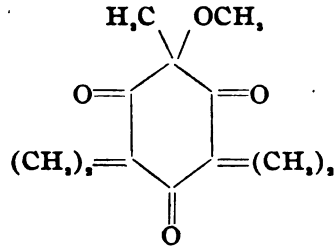
This is formed by the action of ferric chloride on the aqueous solution of sodium tetramethyliretol, two molecules, of which unite, each losing one atom of hydrogen. The precipitation

is attended with a change of color of the solution into deep violet, passing into olive-brown, and finally clear green. It forms white needles, melting at 133°, easily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water. It is very stable, having, in general, the properties of a saturated compound.

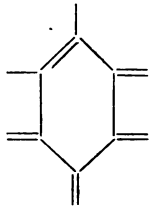
ANALYSIS.

	Per cent. C.	Per cent. H.	Molecular weight.
Calculated for $C_{22}H_{30}O_8$	62.64	7.11	422
Found	62.49	7.14	367

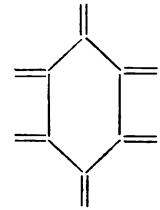
Pentamethyliretol, $C_{12}H_{16}O_4$.—



This is formed by further methylation of the sodium tetramethyliretol by means of methyl iodide. According to this, it is a derivative of tetrahydrobenzene,



and not of hexahydrobenzene.



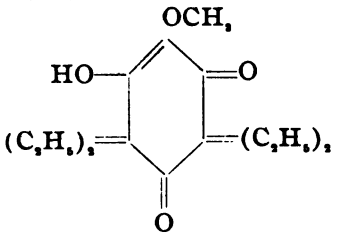
As it has, in general, the properties of a saturated compound, it was thought that rearrangement of the atoms in the molecule of the tetramethyliretol must have taken place in the above process, and this is proved by the methoxyl determination, which shows the presence of but one methoxyl group.

ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. OCH_3.	Molecular weight.
Calculated for $C_{11}H_5(OCH_3)O_3$	63.72	7.97	13.72	226
Found	63.62	7.98	13.63	190

It crystallizes from a methyl alcohol solution in long white needles, melting at 62°, boiling at 240°, and slowly subliming at ordinary temperatures.

Tetraethyliretol, $C_{16}H_{24}O_4$.—



This was prepared similarly to the corresponding methyl compound. That its constitutional formula is analogous to the latter is shown by the methoxyl determination in the following

ANALYSIS.

	Per cent. C.	Per cent. H.	Per cent. OCH_3.
Calculated for $C_{14}H_{21}(OCH_3)O_3$	67.16	8.95	11.57
Found	67.21	9.19	13.81

Its sodium salt being somewhat soluble in caustic soda, it is difficult to isolate from the other products of the reaction, but it may be accomplished by first removing them with ether, when it may be crystallized from the chloroform and acetic ether extraction of the residue by precipitating with ligroin. It forms white, anhydrous prisms, melting at 168°–169°.

Analogous to the trimethylether of phloroglucinol,

$$C_6H_3(OCH_3.1.3.5)_3$$

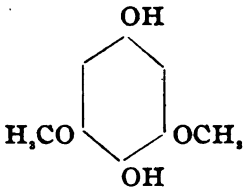
(prepared by saturating the methyl alcohol solution of phloroglucinol with hydrochloric acid gas, and then further methylating the dimethyl product thus formed by using methyl iodide in alkaline solution), we have attempted to prepare the trimethylether of iretol, the tetramethylether of asymmetrical tetroxybenzene, but as yet, without success.

Monomethyliretol, $C_6H_3(OCH_3)_2(OH)_2$.—This is the dimethylether of asymmetrical tetroxybenzene. It is formed by the action of hydrochloric acid gas on the methyl alcohol solution of iretol at 0°. When freshly prepared it is of oily appearance but slowly solidifies to a crystalline mass. When crystallized from boiling benzene it forms white tablets, melting at 87°, easily soluble in

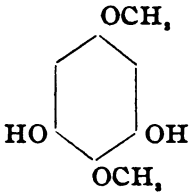
water, alcohol, and ether, but less soluble in benzene and chloroform.

It may be further methylated by the action of methyl iodide on its sodium salt, but instead of obtaining thus a normal asymmetrical tetroxybenzene ether, polymethyl derivatives of methyliretol result, since the methylation takes place in the benzene ring.

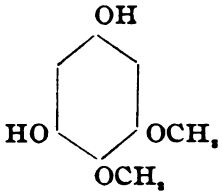
The dimethylether,



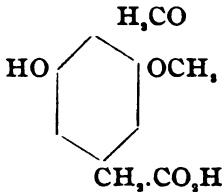
prepared from the unsymmetrical tetroxybenzene differs completely from the monomethyl iretol. Hence, the latter conforms to one of the two formulas:



or



Constitution of Irigenin and Iridin.—Irigenin has the formula $C_{15}H_{16}O_8$. By hydrolysis it takes up three molecules of water and breaks up into

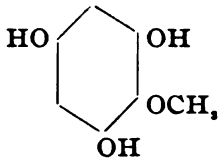


Iridinic acid.

CH_2O_2

Formic acid.

and



Iretol.

Iridin, also, can undergo hydrolysis.

The presence of two phenol groups in irigenin is demonstrated by the formation of the dibenzoylirigenin and the diacetylirigenin; the unstability of diacetyl derivative relative to the

monoacetyl derivative, indicates that these phenol groups are not similarly situated in the irigenin molecule.

We have not yet been able to crystallize the hydrolyzed irigenin, but, by converting it into its potassium or sodium salt (accomplished by treating its absolute alcohol solution with sodium or potassium ethylate) we have thus been able to effect its isolation. From the analysis of these salts is made clear the reaction of the hydrolysis.

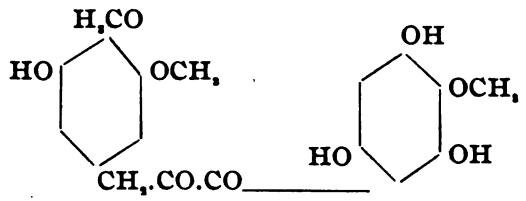
ANALYSIS.

($C_{24}H_{26}K_2O_{14}$ and $C_{24}H_{26}Na_2O_{14}$.)

	Per cent. K.	Per cent. Na.
Calculated	17.96	11.39
Found	18.32	11.69

If, now, instead of using an *excess* of potassium ethylate, only the amount sufficient to form the tribasic salt be taken, a *di*-basic salt is always the result, which indicates that one of the hydroxyl groups of the hydrolyzed irigenin is of a weaker acid character than the other two. Consequently, the first product in the hydrolysis of iridin is $C_{18}H_{14}O_8(OH)_2(OC_6H_{11}O_5)$, and, for irigenin, is $C_{18}H_{14}O_8(OH)_4$.

Since the hydrolyzed irigenin is a relatively sable compound, not being attacked by reagents which effect the saponification of ether, we conclude that the two portions of the irigenin molecule, representing respectively iridinic acid and iretol, are not linked together by an oxygen atom, but are held together by a chain of carbon atoms, as shown in the following formula:



According to this formula, the hydrolyzed irigenin is an α di-ketone. This is further proved by the similarity of its reactions with alkali reagents and those of benzene, the latter, in the presence of potassium cyanide, yielding benzaldehyde, and benzoic acid, while the former yields iridinic acid, or aldehyde, and a carboxyl derivative of iretol.

This is more particularly shown by the formation of the same aldehyde by the decomposition of irigenin, and also synthetically from iretol. In the first case, the hydrolysis of the irigenin was effected by dilute caustic soda. After precipitating with sulphuric acid and filtering, soda solution and potassium cyanide were added to the solution. After standing some eight days, it was acidified and extracted with ether. The aldehyde was separated from the ether extract by sodium bisulphite. By cautiously decomposing with sulphuric acid, and shaking with ether, the aldehyde was obtained as a syrup, which, on digesting six hours with alkali, gave the theoretical amount of formic acid.

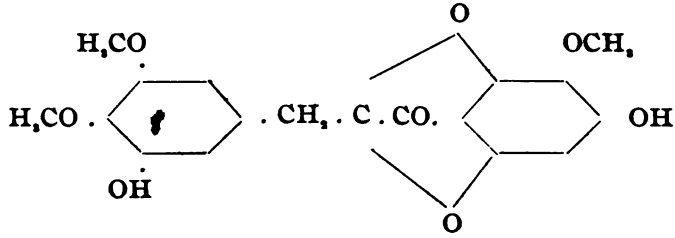
The synthesis of the aldehyde from iretol was effected by the action of chloroform and caustic soda on iretol in an atmosphere of hydrogen. After removing the chloroform by evaporation, the aldehyde was separated as above, it was also, in like manner decomposed, yielding iretol and formic acid.

The hydrolyzed irigenin, by taking up the elements of water, breaks up into iridinic acid and iretol aldehyde, this latter subsequently being converted into iretol and formic acid. Analogous to this is the decomposition of phloroglucinolcarboxylic acid into phloroglucinol and carbon dioxide, by boiling its aqueous solution.

From the foregoing, we feel justified in giving irigenin the formula

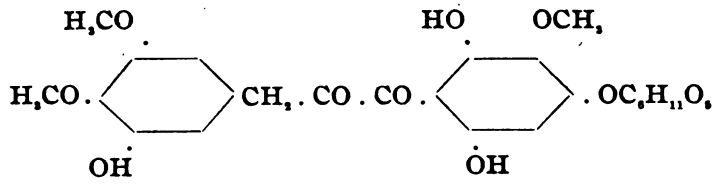
$$(H_3CO)_2(HO)C_6H_2.CH_2.CO.CO.C_6H_2(OCH_3)(OH)_2.$$

The irigenin itself contains one less molecule of water, and, in accord with all the reactions described, has the following constitution:

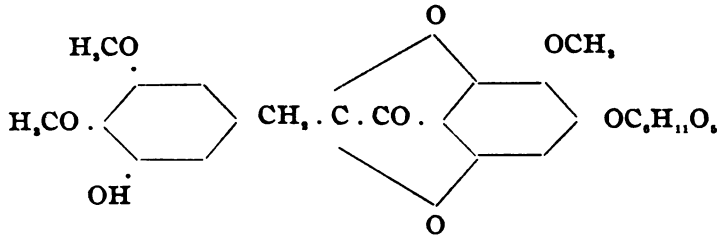


The iridin contains the glucoside residue, $OC_6H_{11}O_5$, in place of one of the two hydroxyls of irigenin.

We have previously noted the weaker acid character of one of the three hydroxyls of hydrolyzed iridin relative to the other two; we have also remarked that in titrating iridinic acid, $(H_3CO)_2.C_6H_2(OH)(CO_2H)$, with caustic soda and litmus, the end-point is obtained as soon as the hydrogen of the carboxyl group has been replaced by the alkali. From these two considerations we conclude that in the hydrolyzed iridin, the hydroxyl having the weakest acid character is found in the iridinic acid nucleus. Consequently, the constitution of hydrolyzed iridin is



Finally, if the above results and conclusions are correct, iridin itself has the constitutional formula



In closing, we would add a word regarding the probable relation of iridin and irigenin to the sugars; both are carbohydrates, and, as without doubt, the sugars are the first products changes of the plant matter, it appears probable that iridin and irigenin are formed from three and four molecules of sugar respectively, by the splitting off of eleven and ten molecules of water. In reviewing the possible methods of the formation of sugars from benzene derivatives, our attention is called to "cyclo" sugars, formed by an aldol condensation between the first and sixth groups of the chain in hexanpentolal

$$\overset{1}{HOC}.\overset{2}{CHOH}.\overset{3}{CHOH}.\overset{4}{CHOH}.\overset{5}{CHOH}.\overset{6}{CH_2OH}.$$

This, perhaps, is the manner in which inosite is formed. Since the pinite occurring in some resins has been proven by L. Maquenne[1] to be the monomethyl ether of an inosite, and, as the latter, by the symmetrical splitting off of three molecules of water, yields phloroglucinol, and the former, by losing two molecules of water, yields dihydroiretol, which can be converted into iretol by the removal of two atoms of hydrogen, the general relation of iridin to the sugars is better understood.

Our thanks are due to Dr. Paul Krüger, and to Dr. Richard Schmidt, for their valuable assistance in prosecuting this investigation.

BOTRYTIS BASSIANA AND ITS CRYSTALLINE PRODUCTS.[2]

By E. Verson.

AMONG the alterations produced by *botrytis bassiana* almost all authors note an abundant crystalline efflorescence which very often covers the small mummified bodies of the muscardin worms.

M. Dandolo in note 21 of his book, "*l' Art d' elever le verf à soie*," 1814, has written on this subject as follows: "As soon as I had observed attentively the worms or muscardin chrysalides I affirmed without hesitation that all this must be the consequence of chemical attractions and combinations."

It was in fact difficult to be mistaken after having seen the animal tissue altered in this manner and converted into a substance more or less hard and unalterable while before it was an animal substance easily decomposed. I put away with care the white saline substance which enveloped the so-called muscardin worms and afterwards analyzed it. Not being satisfied with my work I asked my learned friend, M. Brugnatelli, professor of chemistry at Pavia, to make an analysis of the material.

"The muscardin which covers the mummy of the worm or the chrysalide in the cocoon is composed principally of magnesium ammonium phosphate."

A like opinion was given by M. Lomeni (*Variétés agraires*

[1] *Ann. chim. phys.*, [6], 22, 264.

[2] Read before the World's Congress of Chemists, Thursday, August 24, 1893.

économiques et technologiques, **8**, *1835*), who says: "The chemical analysis of this substance has proved to M. Dandolo and to the late Professor Brugnatelli that the efflorescence of the muscardin is a combination of magnesia, phosphoric acid, and ammonia. Professor Balsamo thinks also that the whitish efflorescence by which the worms are enclosed is entirely inorganic."

Mr. Charles Vittadini in his celebrated work, *Della natura del calcino o mal del segno* (*Journal de l' T. R. Instituto Lombardo di Sc. L. A.*, **3**), expresses an entirely different opinion on this subject.

"The cadavers of the muscardin worms," he says, "after being deprived of their efflorescence and kept in a humid state become covered, after several days, with a second efflorescence which has also the appearance of a muscardin; but this is formed by myriads of fine crystals produced by the final chemical metamorphosis of the cadaver. These crystals observed by the naked eye have the form of diverging bunches of needles like a brush or of rounded masses which resemble the sea-urchin. They are transparent, colorless, or slightly reddish. The crystals dissolved in warm water show a decidedly acid reaction which becomes more sensible by evaporating the solution; on being treated with caustic potash it gives off a strong ammoniacal odor; the geometrical figure consists of long prisms with a rectangular base with cuneiform extremities."

"The reaction obtained by M. Cardoné on a small quantity of the crystals indicates a combination of alloxanic acid and ammonia with small quantities of potassium and calcium. In fact during the new process of crystallization a thick reddish liquid, generally alkaline, of a strong ammoniacal odor, flows off the cadaver of the worm and deposits a considerable quantity of crystals."

This secondary efflorescence, which takes place not only on the surface of the cadaver but extends to all the interior tissues by giving them an almost vitreous appearance, explains to a certain extent the doubt expressed by some observers that the *botrytis* is nothing else than simple crystallization.

I cite only these three authors who agree with what the literature furnishes on the nature and composition of the efflorescence

and do not mention others who have investigated the crystalline efflorescence and its different properties.

The worms mummified by the muscardin, consist always of a plentiful crystalline substance which, dispersed between all the tissues, is accumulated in considerable quantities in the inside of different parts of the somatic cavity. But it is to be remarked that the crystals do not always have the same exterior appearance; this depends on the humidity of the surrounding atmosphere. When kept perfectly dry from the beginning the crystalline substance remains inside of the cutaneous integument and consists of very fine needles which impregnate all the tissues. In an atmosphere more or less humid the cadaver when it begins to dry, exudes on the surface a dense reddish humor, which forms a crust of an earthy appearance. The microscope shows that the exuded substance notwithstanding its amorphous appearance is mostly of a crystalline nature and is not different from the substance left and dispersed between the interior viscera.

Finally, if we place the fresh cadaver in a warm place, more or less closed and saturated with moisture we will see after a certain time the crystallization in the sea-urchin forms which rupture the superficial integument. Often they are disposed without order in different parts of the body but generally are to be found in both extremities and where the visceral volume does not hinder a larger expansion of the somatic cavity.

It is to be remarked that the formation of the sea-urchin crystallizations is not limited to the time immediately following the death of the worm. I was able to obtain it from cadavers mummified some months before by placing and keeping the cadavers during some weeks in a humid warm place. By means of two needles these crystals can be removed from the cadaver like the stone from a dried fruit.

By this method I was able to provide myself with a certain quantity of material though not free from mechanical impurities and of reddish appearance. By dissolving it in warm water, filtering, and concentrating the filtrate at a moderate temperature I obtained a crystalline mass which on being redissolved, recrystallized two or three times, and separated from the mother-liquor, were obtained perfectly pure. I may remark here that

although the warm water is of a moderate temperature (50°-60° C.) the solution of the crystals is always accompanied by the formation of very small bubbles which are probably carbon dioxide; in repeating this operation an insoluble residue always perceptible though very light is noticed. This is the reason which led us to believe that the crystals are not stable and liable to decompose even by dissolving in distilled water. That belief is fortified by the fact that I was never able to obtain the crystals in the sea-urchin form though under the microscope the crust of the second and third crystallization seemed to be composed of ordinary prisms with dihedral extremities.

The crystals of the sea-urchin form are easily soluble in distilled water and react decidedly acid. Dried and heated in a small test-tube which is covered by a piece of paper moistened with litmus solution they produce the following phenomena: without any visible change of appearance, they expel ammoniacal vapors which turn the litmus blue; by further heating they melt to an ash-colored, foamy mass, the bubbles expelling whitish vapors. On the neck of the tube small drops of a condensed liquid can be seen; in the upper part of the test-tube a ring of crystalline needles sublimes; the odor is strong and excites a cough; on the bottom remains a whitish compact residue with little carbon.

The solution obtained from the crystals does not show any change with hydrochloric and sulphuric acids; ammonium chloride, ammonia, and sodium phosphate form an abundant precipitate. Ammonium carbonate and caustic ammonia do not produce any visible reaction.

The solution remains clear on concentrating with platinum chloride or even with potassium antimoniate; calcium hydroxide sets free an abundant quantity of ammoniacal vapors. The residue left from evaporation on the salt-bath dissolved in nitric acid produces some insoluble flocks; the result is almost absolutely negative with molybdic acid.

Another portion of the liquid was treated with barium chloride and gave an abundant precipitate, soluble in hydrochloric acid; a white precipitate is obtained by treating with silver nitrate; calcium chloride gave a white precipitate on being added to the

alkaline solution; ferric chloride precipitates voluminous reddish flocks.

A portion of the solution of crystals obtained was precipitated with lead acetate; the precipitate was decomposed by hydrogen sulphide; the filtered solution after evaporating, left on the bottom rhombic prisms which, on redissolving, produced a white precipitate with calcium chloride insoluble in acetic acid. Heated in a small tube they sublime without residue, while heated with strong sulphuric acid they effervesce and evolve carbon dioxide and carbon monoxide.

Finally I investigated the residue of the calcined crystals of the sea-urchin form. This, when dissolved in hydrochloric acid, does not give any appreciable precipitate unless by adding ammonia, ammonium chloride, and sodium phosphate. After all the reactions I have mentioned above there can not be any doubt about the composition of the crystals. Not taking into consideration the impurities which can not be entirely removed and remain as undeterminable traces of potassium, phosphoric, silicic, and succinic acid, the crystals are composed mostly of *oxalic acid, ammonium, and magnesium.*

I have also determined the percentage composition of the crystals as completely as the small amount of material permitted.

I. Purified crystals, 0.0784 gram; dried at 100° C., 0.0686 gram; difference=0.0098; equal to 12.47 per cent. Dissolving the crystals in distilled water and treating the acidified solution with calcium acetate I obtained by the regular method 0.054 gram calcium carbonate which corresponds to 0.0389 gram oxalic-acid or 49.62 per cent.

II. Purified crystals, 0.2572 gram; dried at 100° C., gave 0.2243 gram; difference 0.0329, equal to 12.80 per cent. Dissolved in distilled water and treated with calcium acetate gave 0.1727 gram calcium carbonate which corresponds to 0.1243 gram oxalic acid or 48.33 per cent.

III. Purified crystals, 0.1571 gram; dried at 100° C., 0.1376 gram; treated with milk of lime (Schloesing's method). After forty-eight hours the ten cc. of normal sulphuric acid was neutralized by only 8.06 cc. of normal caustic soda or 1.94 cc. of

normal sulphuric acid was neutralized by the ammonium of the crystals, which corresponds to 22.23 per cent.

IV. Purified crystals, 0.2560 gram; dried at 100° C., left 0.2243 gram; Schloesing's method for determination of ammonium gave 0.0576 gram of ammonium, equal to 22.50 per cent.

V. Purified crystals, 0.0789 gram; dried at 100° C., left 0.0690 gram. The hydrochloric acid solution precipitated with ammonium chloride, ammonia, and sodium phosphate, gave 0.0066 magnesium pyrophosphate, equal to 0.0015 magnesium or 1.9 per cent.

After the above determinations I conclude that the sea-urchin crystals of the muscardin after being purified by repeated crystallization, contain on an average:

	Per cent.
Water	12.635
Oxalic acid	48.975
Ammonium	22.365
Magnesium	1.900
	85.875

I regret that the amount of material was not sufficient for further investigations in order to find the fourteen per cent. necessary to complete the analysis. We could then establish whether the crystals contain any water which is separated at higher temperature than 100° C. We could also determine the carbon dioxide given off while dissolving the crystals in water and ascertain from comparative analysis the products of different successive crystallizations.

Nevertheless I believe the data we possess are sufficient cause to accept in full certainty that the crystals represent a double salt of oxalate of magnesium and ammonium.

I find described in the literature five double oxalates of the following formula of constitution:[1]

1. $C_2O_4Mg,7C_2O_4(NH_4)_2+8H_2O$.
2. $3(C_2O_4Mg),C_2O_4(NH_4)_2+2H_2O$.
3. $C_2O_4Mg,6C_2O_4(NH_4)_2+9H_2O$.
4. $5(C_2O_4Mg),13C_2O_4(NH_4)_2+H_2O$.
5. $C_2O_4Mg,5C_2O_4(NH_4)_2+10H_2O$.

of which the percentage compositions are as follows:

[1] Souchay et Lenssen, Kayser in *Poggend. Ann.*, 60.

For the first formula:—	Per cent.
Oxalic acid	63.30
Magnesium	1.08
Ammonium	22.66
Water	12.95
	99.99

	For the Second, Per cent.	Third, Per cent.	Fourth, Per cent.	Fifth, Per cent.
Oxalic acid	76.52	61.23	62.26	58.66
Magnesium	7.82	1.19	2.36	1.33
Ammonium	7.82	21.47	18.40	20.00
Water	7.82	16.10	16.98	20.00
	99.98	99.99	100.00	99.99

Comparing the results obtained from our analysis with these figures we have to exclude without hesitation formulas 2 and 4 in which there is a considerably larger amount of magnesium than we have found. Taking into consideration the fact mentioned on the first pages of this investigation, that the crystalline spheres radiated from the muscardin worms are partly decomposed by dissolving in distilled water and the phenomena by which this decomposition is accompanied I believe there is no doubt that the essential cause of the change must be in the oxalic acid.

But as oxalic acid is rapidly diminishing the amount of ammonium and magnesium must increase in the products of each renewed crystallization.

This consideration compels me to lay aside also formulas 1 and 3 and prefer formula 5 as more nearly approaching the results obtained than any of the others.

I have already emphasized at the beginning of this work that the crystals of the sea-urchin form whose nature I have established, are only formed under certain circumstances. But if we enclose the cadaver in a warm and humid place we can on the contrary determine their development at our will.

It seems to me that this fact authorizes us to make a very interesting conjecture; namely, that the immediate action of the *botrytis* is limited to the production of oxalic acid. This remains principally free, being combined generally with very small quantities of lime and magnesia.

But if the surrounding circumstances produce the putrefaction of the cadaver and the development of ammonia, ammonium

oxalate is formed at the same time, which dissolves a certain amount of magnesium oxalate forming the double oxalate; only it then forms that peculiar crystallization to which we wished to confine our attention.

It is very remarkable that *botrytis bassiana* cultivated on nutritive gelatine produces oxalic acid in large quantities which I have separated in a crystalline form.

CLOSING ADDRESS DELIVERED BEFORE THE WORLD'S CONGRESS OF CHEMISTS, AUGUST 26, 1893.

By Albert B. Prescott.

IN this closing hour of the Congress the chair would congratulate its members upon the great interest and value of its transactions. In the wide attendance of European and American chemists, in the weight of the papers in the several divisions of chemical science, in the constant and increasing attendance through the sessions of six crowded days, and in the hearty spirit of brotherly sympathy which has given life and happiness to all our labors, we have been favored beyond the most sanguine expectations. We in the United States know the chemists of Europe better than we did before this Congress. Surely we have the best of encouragement for the union of the chemists of the world in a series of great meetings of profit and acquaintance, the first one of which is now being concluded.

I know that I voice the sentiment of every member when I give our united thanks to those whose active and untiring exertions have carried so well all the arrangements of this meeting. Our thanks are due, first, to the American Chemical Society, who instituted the call for the Congress and now opens its journal to our proceedings. To our general chairman of the joint committee, Professor Wiley, of the United States Department of Agriculture, we have been indebted for most efficient attention in details. He took the position when it was not easy to find one to accept its labors and to face its uncertainties. The chairman of the committee on papers, Professor William McMurtrie, and assuredly the chairman of the committee from the Congress Auxiliary, Professor John H. Long, the local

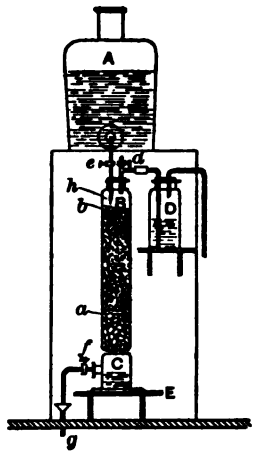
genius of our convention, will be remembered most gratefully by us all. I will not longer detain you from your personal farewells to each other, and now declare the Congress adjourned.

HYDROGEN SULPHIDE GENERATOR.

By H. G. SCHANCHE.

Received September 13, 1894.

THE form of generator shown in the annexed cut has proved itself, during seven years of use, to always furnish an *absolutely uniform supply of gas*. The acid reservoir A delivers the acid into the generator B, containing ferrous sulphide, *a b*, resting on coarse pebbles at *a*. The ferrous chloride collects in C and may be drawn off, from time to time, by opening cocks *d* and *f*, thus allowing it to flow through the lead pipe *g* into a drip-pan underneath the table; D is an ordinary bottle for washing the gas. By regulating the flow of acid by means of the cock *e*, any supply of gas may be obtained, while the height of the column of ferrous sulphide, through which the acid percolates, assures an absolutely uniform supply of gas, as well as a complete neutralization of the acid. The shelf E, on which the generator B rests, can be slipped off its bracket, thus facilitating the removal of B for cleaning or charging.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY, No. 11.]

MODIFICATION OF KNORR'S EXTRACTION APPARATUS.

By OMA CARR.

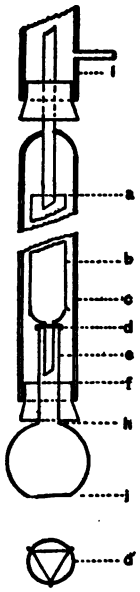
Received October 15, 1894.

TO avoid the inconveniences found with the usual form of mercury seal extractors,[1] such as the expense of flasks, disturbance of the seal by unequal pressures, tendency of the mercury to enter the flask, etc., the modification shown in the drawing is suggested.

The tube a b may be of any convenient size adapted to the

[1] Bulletin, No. 28, Division of Chemistry, p. 97.

inverted percolator-dome c. The top of the flask neck may be simply rounded in the flame, and the small triangle d d' arranged to support the shoulder of the tube a b. The length of the flask between points d and h may be any desired distance, but it is suggested that it protrude above the cork f two inches. The cork f requires no previous extraction, as the solvent in contact with it can not enter the flask containing the extract except by volatilization. The flask may be of any desired size, although the ordinary "sugar flask," of 100 cc. capacity, without rim at the mouth, will be found convenient for the greater range of work.



Where it is desired to complete extract solutions to a definite volume the arrangement will be found particularly useful. The apparatus should be sunk in a water-bath to a depth sufficient to prevent accumulation of the solvent upon the cork f. The apparatus is simple and readily adapted to the condenser of the Knorr extractor, shown at l.

Upon completion of the extraction, the cork f is easily removed and the flask wiped and dried without danger or annoyance caused by mercury globules.

LABORATORY DEVICES.

By Elwyn Waller, Ph.D.

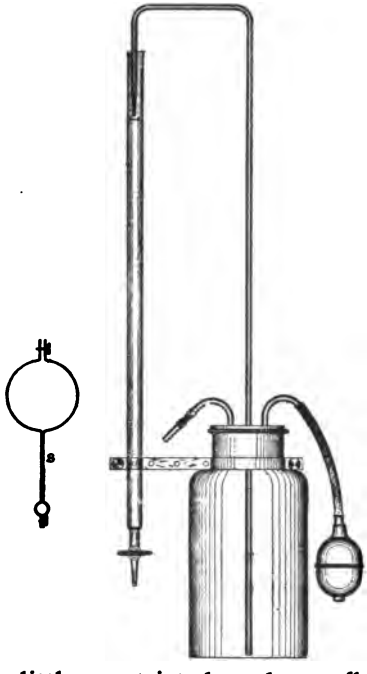
Received October 17, 1894.

DURING the recent general meeting of the Society in Brooklyn, many of the members visited the mineral water establishment of Dr. C. H. Schultz, in New York, and enjoyed his hospitality. After the lunch, the different parts of the plant were inspected by the visitors. In the analytical laboratory were a few forms of apparatus which attracted much attention as they have heretofore not been described. These were the burette-filling device, designed by Dr. A. P. Hallock, the chemist of the factory, the condenser and revolving Nessler rack, adapted by E. W. Martin, of the New York Health Department, and the Nessler comparator as improved by Dr. Hallock.

A description of these may be of service.

BURETTE FILLER.

Around the neck of a bottle of convenient size for the stock solution (capacity two liters or more) is fixed a collar of brass, carrying a clamp for the burette. The collar and clamp are made of two strips of brass bent as shown in the sketch, which are soldered or riveted together at s. The ends are turned outward, and fitted with thumb-screws, to allow the circles to be clamped firmly about the bottle neck and the burette.



The (rubber) cork of the bottle is pierced with three holes. Through one of these passes a tube extending from near the bottom of the bottle to above the top of the burette, then, turning twice at right angles it dips into the burette, being steadied in position there by a cork with a small slit on one side, or fitting loosely. The end of this tube is a little constricted, and cut off at a point corresponding with the zero line of the burette graduation.

Through another hole in the cork passes a short tube connected with an ordinary syringe compression bulb, by means of which air can be forced into the top of the bottle.

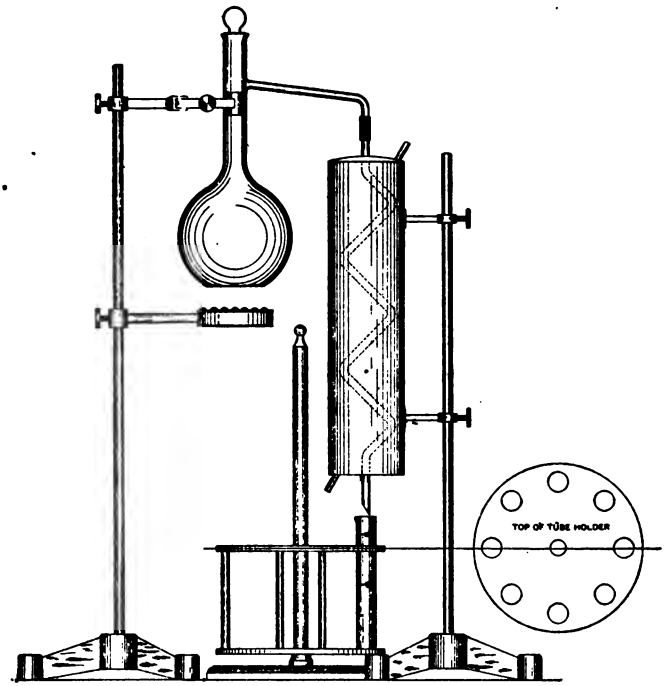
Through the third hole passes another short glass tube, the external end preferably bent downward, so that it may be easily closed by the finger when it may be desired to compress the air in the bottle, or by taking the finger away, the pressure may be at once released.

When it is desired to fill the burette, by closing the air-tube with the finger, and squeezing the bulb a few times, the stock solution is forced over into the burette. As soon as the level of the liquid has come to or above the zero line, the air pressure is released by removing the finger, and all the liquid above the

zero mark siphons back into the stock bottle, leaving the burette filled to the zero mark and ready for use.

The device is simple and comparatively inexpensive, and it has the great advantage that the delivery ("nose") of the burette can be easily fixed at a convenient height above the working table.

Serious objections to most other forms of apparatus constructed for this purpose are, that the delivery of the burette is too high above the working table, or that the stock-bottle has to be fixed



in some elevated position, or that the form of burette which must be used is an elaborate and costly piece of glass-blowing.

CONDENSER.

For water analysis distillations, etc., a glass-stoppered flask with side-neck tube is used. The end of the side-neck tube is turned vertically downward, being thrust deeply into the tin tube of the condenser, and held in place there by a short piece

of rubber tubing. The three-eighths inch block tin pipe forming the condenser-tube is bent zigzag instead of in the conventional helix. This affords a more even flow of the distillate. The cylindrical copper jacket containing the water for cooling is about four inches in diameter, and fifteen inches long. The disk closing the lower end is *arched upward* so that in case the condenser "sweats" from the use of very cold water, the drip from the outside can not contaminate the distillate. The lower end of the tin tube is cut aslant for the more certain delivery of the distillate.

REVOLVING NESSLER STAND.

This is simply a whirligig rack made of two circles of thin board connected with light strips of wood, the upper circle perforated to carry eight or ten tubes, the lower partly perforated to form shallow sockets for the tubes. The rack revolves about an upright set in a base. With such a stand as this, if one tube in the rack is placed in position to receive the drip from the condenser, revolving the rack will bring successively every other tube on the stand into the same position. The danger of upsetting or breaking the tubes is practically eliminated, and, moreover, the order in which the fractions of the distillate are taken off is easily preserved.

NESSLER COMPARATOR.

This has the form of a large test-tube rack of wood, painted black.

At the bottom is placed a strip of milk glass, extending from end to end, held in place by small pieces of rubber (ends of a small rubber cork) fastened to each side by small screws. The edges of the rubber are put so close to the bottom board that the glass can be just forced in between, and when in place it is firmly held.

About two inches above this is a strip of clear glass resting on cleats at the sides of the rack, fixed in place in the same manner as above described, and upon this clear glass the Nessler tubes stand. The necessity for raising the tubes from the white background, in order to make a comparison is thus obviated, and the whole apparatus may be very readily cleaned and kept in

condition. The drawbacks in the use of white paper for a background which may be easily wetted or stained are removed.

It has been found convenient to use a rack of ten or twelve holes, since with that the standards can be placed in every other hole, leaving the vacant spaces for the tubes to be compared.

NEW BOOKS.

LESSONS IN QUALITATIVE AND VOLUMETRIC CHEMICAL ANALYSIS FOR THE USE OF PHYSICIANS, PHARMACISTS, AND STUDENTS. BY DR. CHAS. O. CURTMAN; INCLUDING LESSONS IN QUALITATIVE CHEMICAL ANALYSIS, BY DR. F. BEILSTEIN. Fourth edition. St. Louis, Mo.: John L. Boland Book and Stationery Company. 1894. Price $1.50.

This new edition of a work intended primarily for students of medicine and pharmacy, contains chapters on manipulations of chemical apparatus, qualitative analysis (inorganic), examples for practice in the analysis of organic substances (proximate), volumetric analysis, examination of drinking water, and urine analysis. The author says the section on volumetric analysis "contains numerous examples illustrating every important volumetric method and forms a complete commentary on the volumetric assays of the new U. S. Pharmacopeia." The book contains a number of cuts illustrating various forms of apparatus, urinary sediments, several pathologic micro-organisms, and two charts of spectra. Meyer and Seubert's atomic weights are used. "The orthography has been adapted to the rules of the Chemical Section of the A. A. A. S."

To cover so large a part of the domain of analytical chemistry within a space of 300 octavo pages has required the constant and severe abridgment of methods allowing no opportunity for a discussion of their merits. The author has accomplished his purpose with more than ordinary success. As a rule he has shown excellent discrimination in the choice of methods, and has in some cases introduced matter one would hardly expect to find in so small a work, *e. g.*, Gutzeit's, Fleitmann's, and Bettendorf's tests for arsenic. Physicians and pharmacists will doubtless find the work a useful one. In some cases brevity of treatment has led to dogmatic statements that are liable to be wrongly interpreted by those having little knowledge of the subject under

discussion. Examples of this kind may be found in the chapter on the examination of drinking water. One having had experience in the matter would hardly be willing to state that "albuminoid ammonia may be considered as *proof of sewage actually present*, etc.," p. 244,—the italics are the authors. Other examples of a similar kind might be quoted. Standards of organic impurity in drinking water—a dangerous subject even for experts—can not be arbitrarily established, and the wise analyst will express a positive opinion only as he knows the history of the sample of water under examination. W. W. DANIELLS.

LABORATORY MANUAL OF ELEMENTARY CHEMICAL PHYSIOLOGY AND URINE ANALYSIS. BY JOHN H. LONG, M.D., Sc.D., PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES IN THE SCHOOL OF MEDICINE AND PHARMACY OF NORTHWESTERN UNIVERSITY. Small 8 vo., pp. 360 and index. Chicago: E. H. Colegrove & Co. Price, $2.50.

This work is a decided departure from the methods of the laboratory text-books usually offered to medical students. It joins the exercises in physiologic chemistry with those of applied medical chemistry, a plan that will increase the interest and value of the course. All through the book we find evidence that it is written from practical experience and is an evolution of years of teaching.

In the preface Dr. Long discusses briefly the unsatisfactory state of teaching at medical schools. He expresses the feeling growing among those engaged in teaching chemistry at such schools, that the general principles of the science should be made an entrance requirement.

The first part of the book, one hundred and seventy pages, comprises the chemical physiology. Methods of investigation are presented in considerable detail. Especially noticeable is the essay on polarimetry. Reference occurs as frequently in organic chemistry and physiology to rotation of the polarized ray, and the phenomenon is now recognized as having so direct a relation to molecular structure, that it is wise to give it full explanation. Numerous illustrations of the form and action of polarizing apparatus are given.

Part II, on Urine Analysis, comprises over one hundred and

sixty pages, and includes all that is required for the medical course.

We must express a regret that the spelling is old-fashioned. A teacher in a medical school may be excused from going to the full length of using "sulfate," "sulfid," etc., since the new pharmacopeia has refused to adopt these forms, but the useless final "e" might be dropped in many cases, and general usage permits the abandonment of the diphthong "æ" in all English words. We should prefer, therefore, "hemin" to "hæmin." It is pleasing to note that the approved term "glycerol" is used.

Several useful tables are included in appendix.

There are numerous illustrations of apparatus and of microscopic appearances of important structures. The work will be of great service in the field to which it is devoted. H. L.

THE CHEMISTRY OF PAPER-MAKING. TOGETHER WITH THE PRINCIPLES OF GENERAL CHEMISTRY. A HANDBOOK FOR THE STUDENT AND MANUFACTURER. BY R. B. GRIFFIN AND A. D. LITTLE. 8 vo. pp. 517, 99 illustrations. New York: Howard Lockwood & Co. 1894. Price, $5.00.

The scope of this book is sufficiently indicated in the title. One hundred of the opening pages are devoted to elementary chemistry, evidently intended for the manufacturer who knows little chemistry or has forgotten it; perhaps this was necessary; for chemists who buy the book it is certainly superfluous. Regarding the remaining pages it may be said that the authors display practical as well as theoretical knowledge of the subject, and the result is an entirely satisfactory treatment. They seem to be investigators as well and have embodied in nearly every section some valuable matter derived from their own experience. This will is especially true of those sections of the book treating of the chemical analysis and of paper-testing, which, to most chemists, prove its most valuable features. The treatment of these sections is thoroughly common sense and shows both knowledge and good judgment. Fourteen pages are given to an account of cellulose and its derivatives and their properties; then we have thirty-four pages on the various fibers. Following this, seven pages are devoted to an account of the processes for isolating cellulose. Seventeen pages are given to the soda process,

one page to the sulphate process, and nearly 200 pages to the sulphite process. Next comes Bleaching, twenty-six pages; Sizing and Loading, nineteen pages; Coloring, nine pages; Water, nineteen pages; Chemical Analysis, seventy-two pages; Paper-Testing, thirty-two pages; Electrolytic processes, eleven pages, and an appendix and index. Among other things, the appendix contains an account of the interesting thiocarbonates of cellulose discovered by Cross and Bevan, and a list of United States patents relating to the sulphite process. In brief, the book is an excellent one: well written, well printed, and well illustrated, and worthy of a place on the book-shelf of the chemist.

E. H.

A SHORT HISTORY OF CHEMISTRY. By F. P. VENABLE, PH.D. 12 mo. pp. viii; 163. Boston: D. C. Heath & Co. 1894. Price, $1.00.

The author, who is Professor of Chemistry in the University of North Carolina, has, for several years, given lectures to his students on the history of chemistry, and this little volume is an outgrowth of those lectures. The subject is divided into six Parts: I the Genesis of Chemistry; II. The Alchemists; III. Qualitative Chemistry; IV. Quantitative Chemistry; V. Structural Chemistry; VI. Special Branches of Chemistry. Each Part is subdivided into unnumbered sections and paragraphs, with headings in bold-faced type, making the book convenient for study.

Considering the limited space in the book, the author has certainly arranged an accurate compendium for chemical students, covering the entire field. He shows knowledge of the standard works on historical chemistry in three languages, but he appears not to have access to the earlier original works, except in a few instances. Viewed in the light of the original writings of the zealous alchemists, the iatro-chemists, and the learned philosophers of the last century, the history of chemistry becomes as fascinating as a romance, and a work based on them acquires an individuality which is only partly reflected in a compilation at second-hand.

We notice that high honor is paid to the erudition of the Arabian chemist, Geber, notwithstanding Berthelot has shown that the writings usually ascribed to Geber can not be traced

back farther than the beginning of the XIII century, and that they never did exist in Arabic; the MSS. said to be found in the Paris Bibliotheque Nationale and which have been translated into Latin and modern languages are fictitious.

In a larger part of the volume the subject is treated in a series of biographies; this, however, is natural where the discoveries of certain individuals exerted radical changes in the philosophy of the science.

In Parts IV and V the development of modern chemistry is well set forth, and every student of the science would do well to read and absorb these chapters early in his curriculum.

Professor Venable names a chemical periodical established as early as 1697 by Stahl.

An excellent feature of the work is its fair-mindedness, giving credit where credit is due. This remark is, perhaps, superfluous, as the book is American; but after Jagnaux' great volumes, written to prove that chemistry is a French science and the polemical writings of certain German authors, one can not but recognize the impartiality characteristic of American writers.

A few illustrations, portraits, and representations of original apparatus would have enlivened the volume; perhaps these can be introduced in a second edition. The proof-reading is excellent. There is an index. H. C. BOLTON.

QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS. BY DR. ALEXANDER CLASSEN. AUTHORIZED TRANSLATION, SECOND ENGLISH, FROM THE THIRD GERMAN EDITION, REVISED AND GREATLY ENLARGED. BY W. H. HERRICK, A. M. New York: John Wiley & Sons. 1894. Price $3.00.

It is now twelve years since Professor Classen published the first edition of this book. The little volume of about fifty pages contained a systematic description of the methods then practiced in the laboratory at Aachen, little or no attempt being made to include the results that had been obtained elsewhere. An entirely rewritten and much enlarged second edition was issued in 18 6. In this, electrolytic analysis is treated as an independent branch of quantitative analysis, but while the methods proposed and worked out by the author and his associates are fully presented, only occasional reference is made to the researches of

other experimenters: "Nach eignen Methoden," still remained the device of the book.

A third edition, of which the subject of this review is a translation, appeared in 1893. The author now evidently attempts to present a complete treatise on electrolytic analysis. The numerous controversies with other chemists, and the adverse criticism of some of his methods, have induced him to revise and modify considerable portions of the text, and to introduce many methods developed and described by others. Nevertheless the book is not entirely free from the defects of its earlier editions. Especially is it to be regretted that Prof. Classen has not thought it worth his while to give references to the original papers.

The most satisfactory part of the work comprises the introductory chapters; the descriptions of the apparatus used for generating, reducing, and measuring the current are very complete, and leave little to be desired. The Gilcher thermopile might, perhaps, have replaced the older constructions, and some of the obsolete forms of galvanic cells might have been omitted. The translator has made some very judicious additions, describing devices used in American laboratories.

Under "Determination of the Metals" much new matter has been introduced. Great stress is laid upon the proper control of the current, and, whenever possible, the normal density is given. Most of the space is allotted to the precipitation of metals from solutions of their double oxalates, and it is tacitly assumed, that this is in most cases the best method. Prominence is also given to the electrolysis of the sulphosalts of antimony and tin—a method improved by Classen—and the deposition of metals from solutions of their pyrophosphates (Brand). The names of Smith and Rüdorff appear very frequently, but we do not find that the directions for carrying out their processes are always adequate, and not a few of the American chemists' methods are entirely omitted.'

This criticism applies even more strongly to the section on the separation of the metals. While excellent results are doubtless to be obtained by the use of many of the methods described here, it can not be denied that some are not separations at all (iron from cobalt, nickel, and zinc, etc.), and others are not

electrolytic separations. It seems to us that in many cases the author could have substituted, with advantage, the electrolytic processes, which have been proposed by others in recent years.

Professor Herrick's translation is excellent in every respect; while it closely follows the original text, it contains numerous very valuable additions. H. F. KELLER.

LABORATORY MANUAL AND PRINCIPLES OF CHEMISTRY FOR BEGINNERS. BY GEORGE M. RICHARDSON, ASSOCIATE PROFESSOR OF CHEMISTRY IN THE LELAND STANFORD JUNIOR UNIVERSITY. pp. 233. New York: Macmillan & Co. 1894. Price $1.10.

This book is, as the author states in his preface, "principally intended as a *laboratory manual*," and the course of experiments "arranged for the elementary students of chemistry in this university." It is in two parts, Part I (pp. 84) consisting of a course of laboratory experiments, and Part II being devoted to theoretical chemistry.

While many of the laboratory experiments contained in Part I are instructive and well adapted for their purpose, and well suited for beginners, there are also many with which fault may be found.

In some instances these experiments involve the use of rather complicated pieces of apparatus requiring an expenditure of the student's time to get together and set up which is out of proportion to the importance of the fact to be taught by the experiment itself; in other instances the time and work required to perform the experiment are in like manner excessive when taken in comparison with the importance of its object.

But a far more serious fault than this lies in the difficulty of most of the quantitative experiments, of which there is a very considerable number, "greater," as the author states, "than is commonly found in such laboratory manuals."

Most of these quantitative experiments are decidedly beyond the ability of the average beginner in chemistry to perform with any degree of accuracy, and some of them can yield accurate results only in skilled hands.

It is far worse than useless to require a student to perform quantitative experiments without also requiring of him accurate results; hence, if quantitative work is to be given to the beginner

at all; in itself a matter of more than doubtful expediency; the experiments given him should be of the simplest kind only, and of such a nature that even in inexperienced hands, fairly accurate results may be obtained.

The requirement from students of quantitative work, the proper performance of which lies beyond their abilities, is almost inevitably followed by one of two consequences—the conscientious student, failing after repeated attempts to obtain correct results from an experiment, is apt to become discouraged, and begins to dislike his work; his less conscientious fellow, tiring of an experiment after he has repeated it once or twice, "cooks" his figures to give the desired result in order to get rid of it. In either case the harm done is great.

In Part II, "the writer has attempted to give a clear and concise statement of some of the fundamental theories and principles of chemistry; here he has gone more into detail than is customary in books designed for elemetary students."

This part is open to a similar criticism. Some of the matter it contains might be read with advantage by a beginner, but it is not in such form as to be readily available, and the consideration of such subjects as Absolute Temperature, The Determination of Molecular and Atomic Weights, The Determination of Formulas, The Kinetic Theory of Gases, etc., can scarcely be undertaken with profit by beginners in chemistry, and is also rather out of place in a book "principally intended as a laboratory manual."

On the whole, while with some revision the book would be an excellent one to place in the hands of a second-year student, it is hardly one which can be recommended for the use of beginners.

R. D. C.

NOTES.

International Chemical Congresses.—The following circular letter has been addressed to the foreign chemical societies:

DEAR SIR:

An International Congress of Chemists, organized in connection with the World's Columbian Exposition, was held at Chicago in August, 1893. The American Chemical Society met

conjointly with the Congress, and, on account of the interest which was manifested, appointed a Committee of Conference to consider the expediency of holding similar congresses at regularly recurrent intervals of time. The geologists have established a series of International Congresses, which meet triennially; in medicine and pharmacy similar organizations exist; and in each case the success of the meetings has been very great. The undersigned, therefore, representing the American Chemical Society, respectfully request the chemical societies of the world to appoint similar committees of conference, in order to consider whether it is desirable and practicable to organize a series of International Chemical Congresses, in which the chemists of the various nations can regularly meet together for the discussion of questions of common interest. Hoping for a favorable response, we remain, in behalf of the American Chemical Society,

Very respectfully,

(Signed,) F. W. CLARKE,
CHARLES E. MUNROE,
H. CARRINGTON BOLTON,
EDWARD HART,
W. O. ATWATER.

Please address reply to F. W. Clarke, U. S. Geological Survey, Washington, D. C., U. S. A.

Soldering Aluminum.—Professor Joseph Richards contributes an article on this subject to the first number of the *Aluminum World* from which we learn that the best results have been obtained from an alloy of zinc, tin, aluminum and *phosphorus*. "This solder can be used before the blowpipe or with a soldering iron. In the former case, a little silver can be added to it without making it too hard to melt, and giving it a better color. For use with the copper bolt, this solder leaves little to be desired. The surfaces to be united are first scraped clean, and then tinned with the solder itself by rubbing it on hard with the bolt. The prepared edges are then soldered together with ease, using a hot iron and no flux of any description."

Pure tin, or an alloy of tin and aluminum will solder, but the joints become brittle. Zinc and cadmium are useless because too brittle. Silver chloride attacks aluminum depositing silver,

and the surfaces thus formed may be soldered, but the material is too costly. Cadmium chloride can be used only when dry, and is a deliquescent salt. The Alsite aluminum solder is used only with the blowpipe; its composition is not divulged, and the melting-point is dangerously near that of aluminum. Electroplating the surfaces to be soldered is not satisfactory as the plating peels when subjected to heat. E. H.

Note on a Device for Weighing Oil for Analysis.—The following device I have for some time used, and found to be so convenient and simple, that I give a description of it hoping that it may be of service to others. It consists simply of a small glass evaporating dish, about one inch in diameter, supported upon a flat watch-glass. An amount of oil, greater than the amount desired for the experiment, is placed in the evaporating dish and the whole weighed. The proper amount of oil is then poured from the dish into the vessel in which it is to be analyzed, and its weight determined by difference. If a drop of oil should cling to the lip of the evaporating dish and run down on the outside, it will be caught by the watch-glass and will occasion no trouble. The whole affair costs but a few cents and may be cleaned with great ease, while for weighing oil it is quite as accurate as a weighing pipette.

November 5, 1894. PARKER C. MCILHINEY.

ERRATA.—Page 348, May, 1894, ninth line from top of page, after the words *violent bumping*, insert *ninety cc. of water is now added.*

Page 349, May, 1894, in the last two lines, for *Cengola* read *Angola.*

Index to Vol. XVI, 1894.

ACETONE, contraction of aqueous solutions of..... 618
Address by Dr. H. W. Wiley..... 1
Agricultural chemists, Washington meeting of (note)..... 431
Agricultural Report of Nebraska for 1853 (book review)..... 573
Air-Bath, new form of..... 31
AITKEN, A. P. A Rapid and Accurate Method of Determining the Moisture and Oil in Linseed Cakes and Other Feeding Stuffs..... 114
Albumen in cow's milk, determination of..... 712
Alloys of lead and tin and lead and antimony, valuation of..... 541
Alum, aluminum hydroxide and aluminum phosphate, influence on digestibility of bread..... 587
Alumina, remarks about basic sulphate of..... 153
Aluminum, notes on, 485; soldering (note)..... 880
ANDREWS, GEORGE FREDERICK. Notes on Aluminum..... 485
Arsenic tests of U. S. Pharmacopeia..... 580
Arsenopyrite, chemical behavior of..... 624
Assaying, manual of (book review) 142; loss of gold and silver in scorification assay, 313; accuracy of the commercial assay for silver, 505; with the blowpipe (book review)..... 571
Ash analysis, changes in official methods of (note)..... 792
Asphaltum, technical analysis of..... 809
Atmospheric element, a new (note)..... 719
Atomic weights, report of committee on..... 179

BALANCE, device for adjustment of, 699; safety attachment for riders..... 764
Baltimore meeting, the..... 73
Barium and strontium, occurrence in silicate rocks, 81; estimation of small amounts of 83
BASKERVILLE, CHARLES. Separation of Titanium from Iron, 427; Separation of Zirconium by Means of Sulphurous Acid..... 475
BEAL, W. H. The Determination of Volatile and Insoluble Fatty Acids in Butter Fat. 673
Bean, proteids of kidney..... 633, 703, 757
BEESON, J. L. Notes on the Estimation of Crude Fiber in Sugar Cane..... 308
Benzene in illuminating gas, determination of..... 697
Beryl, analyses of..... 65
Biochemistry, importance of the study of..... 261
BICKNELL, G. H. See Cremer, J. H.
BISHOP, H. A. Hydrogen Sulphide Generator..... 48
BIGELOW, W. D., and C. C. Hamilton. The Influence of Alum, Aluminum Hydroxide, and Aluminum Phosphate on the Digestibility of Bread..... 587
BLINKS, W. M. See Noyes, W. A.
Blowpipe, assaying with (book review)..... 571
Borax, volatility of..... 410
Boric acid works at Lardarelo, the..... 538
Botrytis bassiana, products of..... 860
BOWMAN, J. W. See Mason, W. P.
BRADBURY, ROBERT H. On the Reaction Between Molybdic Acid and Potassium Chromate and Bichromate..... 565

Brasses, analysis of..... 133
Bread containing alum, etc., digestibility of..... 587
Bronze, analysis of..... 133
Brooklyn meeting (announcement)..... 575
BRYANT, A. P. See Day, Wm. C.
Burette, an automatic zero..... 145
Burette clamp, a convenient (note)..... 719
Burette filler..... 870
BURR, HENRY C. See Smith, Edgar F.
BUSH, CHARLES S. Degras..... 535
Butter, determination of fatty acids in..... 673

CALCIUM bromide and iodide, hydration of..... 621
Calcium oxide, determination in quicklime..... 721
California wines, analyses of..... 597
CAMPBELL, E. D. Determination of Nickel in Nickel-Steel..... 96
Candle material, melting-point and composition of..... 825
Carbonic acid, apparatus for estimation of..... 204
CARR, OMA. Modification of Knorr's Extraction Apparatus..... 868
Cattle foods, recent progress in analysis of..... 174
Cement, chemical and physical examination of.....161, 283, 323, 374
Cerium, contributions to the chemistry of..... 649
Chemical and Metallurgical Handbook, Cremer and Bicknell (book review)..... 790
Chemistry teaching, quantitative work for beginners in chemistry, W. A. Noyes..... 59
Chlorine, estimation in water (note)..... 71
Clamp for burette, convenient (note)..... 719
CLARKE, F. W. Report of Committee on Determinations of Atomic Weights Published during 1893..... 179
CLASSEN, ALEXANDER. Quantitative Chemical Analysis by Electrolysis (book review)..... 877
Closing address before World's Congress of chemists..... 867
Condenser..... 871
Congresses, International Chemical (note)..... 880
Copper, analysis of.....65, 133, 785
Cream of tartar substitutes, analysis of..... 333
CREMER, J. H., and G. A. Bicknell. Chemical and Metallurgical Handbook, (book review)..... 790
CROBAUGH, FRANK L. Experiments on the Estimation of Graphite in Pig Metal.... 104
CROOKES, WM. Select Methods in Chemical Analysis (book review)..... 789
CROSSMAN, TOM. The Analysis of Malt..... 559
CURTMAN, CHARLES O. On Some of the Arsenic Tests of the U. S. Pharmacopeia (1890), 580; On the Hydration of Calcium Bromide and Iodide, 621; On the Quality of Potassium Iodide Sold in the Market as U. S. P., 678; Lessons in Qualitative and Volumetric Analysis (book review)..... 873
CUSHMAN, B. S. See Dennis, L. M.

DAVOLL, DAVID L., JR. Fallacies of Post-Mortem Tests for Morphine..... 799
DAVY, HUMPHREY. The Decomposition of the Fixed Alkalies and Alkaline Earths (book review)..... 717
DAY, DAVID T. Mineral Resources for 1893 (book review)..... 572
DAY, WM. C., and A. P. Bryant. Note on Pemberton's Method of Phosphoric Acid Determination as Compared with the Official Methods..... 282
DE BENNEVILLE, JAMES S. Laboratory Notes, 65; Experiments on the Analysis of Pig Copper, Brasses and Bronzes, 133; Experiments on a Ferro-Tungsten, 297; Some Alloys of Iron with Molybdenum, Tungsten, and Chromium as Solutions.. 735
DEWEY, F. P. The Accuracy of the Commercial Assay for Silver..... 505
Degras..... 535

De Koninck, L. L. A New Hydrogen Sulphide Generator Specially Adapted for Use in Analytical Laboratories..... 63
De Laire, G., and Ferd. Tiemann. Iridin, the Glucoside of the Iris Root..... 847
Dennis, L. M., and B. S. Cushman. On the Analytical Properties of Iron Phosphide and Phosphate..... 477
Dennis, L. M., and W. H. Magee. Contributions to the Chemistry of Cerium..... 649
De Schweinitz, E. A. The Importance of the Study of Biochemistry..... 261
Distillations, method for conducting a number of..... 150
Doolittle, O. S., and Alban Eavenson. Notes and Queries on Dr. Dudley's Method of Determining Phosphorus in Steel..... 234
Dudley, Chas. B., and F. N. Pease. An Attempt to Find the Amount of Phosphorus in Three Samples of Steel, 217; On Some Points in the Determination of Phosphorus in Steel by the Volumetric Method..... 224
Dudley, W. L. The Opening of the Kent Chemical Laboratory of the University of Chicago (note)..... 213

Eavenson, Alban. See Doolittle, O. S.
Eddy, Harrison P. Sewage Disposal at Worcester, Mass..... 682
Electro-chemical Analysis (book review)..... 574
Electrolysis, use of, in technical chemical processes, 49; analysis by (book review). 877
Electrolytic separations..... 93, 420
Elementary Manual of Chemistry, Storer and Lindsay (book review)..... 644
Element, new atmospheric (note)..... 719
Elliott, A. H. Qualitative Analysis (book review)..... 429
Errata..... 288, 648, 792, 882
Expert testimony..... 273
Extraction apparatus, modification of Knorr's..... 868

Fats and resins, new method of analyzing, 275; iodine figure of fats, 372; Koettstorfer figure of dark-colored..... 408
Fatty acids, determination of freezing-point, 665; in butter, determination, 673; for candles, melting-point of..... 825
Ferguson. A Compressed Air Wash-Bottle, 148; An Arrangement for Conducting a Number of Laboratory Distillations with Steam Simultaneously, 150; A Few Remarks About Basic Sulphate of Alumina..... 153
Fermentation of glucose syrups..... 808
Ferric chloride, speed of reduction by stannous chloride..... 314
Ferro-tungsten, experiments on..... 297
Fiber, note on estimation of crude, in sugar cane..... 308
Field, Walter D. Pyroxylin, Its Manufacture and Applications..... 487, 543
Filter disk, an improved..... 58
Fletcher, E. L. Practical Instructions in Quantitative Assaying with the Blowpipe (book review)..... 571
Foods, recent progress in analysis of cattle..... 174
Forbes, Robert H. A Convenient Form of Apparatus for the Estimation of Carbonic Acid..... 204
Fractional distillation, apparatus for..... 160
Frankforter, G. B. The Iodides of Narceine..... 361
Frohman, E. D. See Noyes, W. A.
Fruit, mineral residues in sprayed (note)..... 71
Furman, H. Van F. A Manual of Practical Assaying (book review)..... 142

Garrigues, W. E. On the Gunning Method for Total Nitrogen in Fertilizers, 795; The Determinations of Melting-Points and the Composition of Some Candle Material, 825; Nitrogen in Fertilizers, Gunning Method for Determination of..... 795
Gem stones, specific gravities of some..... 205
Gilchrist, Peter S. Improvements in the Manufacture of Sulphuric Acid..... 498
Gill, Augustus H. On the Determination of Nitrates in Potable Water..... 122, 193

GIRD, W. K. A Gravimeter for Sugar Analysis..... 677
GLADDING, THOMAS S. On the Estimation of Sulphur in Pyrites..... 398
Glass, scale of hardness for 406
Glucose syrups, fermentation of 808
Gold, loss in scorification assay 313
Graphite, estimation in pig-metal..... 104
Gravimeter for sugar analysis..... 677
GREEN, FRANK T. A Device for the Adjustment of a Balance..... 699
GREINER, EMIL. A New Automatic Pipette..... 643
GRIFFIN and Little. The Chemistry of Paper-Making (book review) 875

HALE, A. C. Circular of Announcements for Brooklyn Meeting..... 575
HAMILTON, C. C. See Bigelow, W. D.
HANCOCK, DAVID. Preparation of Standard Iodine Solutions (note)..... 431
Handbook, Bicknell and Cremer, Chemical and Metallurgical (book review)..... 790
HANDY, JAMES O. The Exact Determination of Phosphorus by the Molybdate Method in Iron, Steel, and Ores Which Contain Arsenic..... 231
HIBBS, JOS. G., and Edgar F. Smith. Action of Metallic Magnesium upon Manganous Salts, 822; See also Smith, Edgar F.
HILGARD, E. W. The Chemical and Physical Investigation of Soils..... 34
HILLEBRAND, W. F. The Wide-Spread Occurrence of Barium and Strontium in Silicate Rocks, 81; The Estimation of Small Amounts of Barium and Strontium in Silicate Analysis, 83; A Plea for Greater Completeness in Chemical Rock Analysis 90
History of Chemistry, Short (book review)..... 876
HORTON, HORACE E. Fermentation of Glucose Syrups..... 808
HOWE, JAMES LEWIS. Ruthenium and its Nitrosochlorides..... 388
Humus, notes on Grandeau method for determination of..... 210
Hydrochloric Acid, action on sodium vanadate..... 578
Hydrogen Sulphide Generators.....48, 63, 868

ILLUMINATING gas, determination of benzene in 697
International standards for analysis of iron and steel.....140, 286
Iodine solution, for determining sulphur (calculation), 112; preparation of standard (note)..... 431
Iridin 847
Iron and steel, Committee on International standards for the analysis of..... 140, 286
Iron phosphide and phosphate, analytical properties of..... 477
Iron, separation from titanium 427

JOHNSON, S. W. The Determination of Phosphoric Acid..... 462

KAEHLER, MAX. An Improved Filter-Disk 58
KAHLENBERG, LOUIS. On the Speed of Reduction of Ferrous Chloride by Stannous Chloride 324
KEDZIE, R. C. Mineral Residues in Sprayed Fruit (note)..... 71
KELLER, HARRY F. On the Analysis of American Refined Copper, 785; Some Recent Contributions to our Knowledge of Metallic Reducing Agents..... 833
Kent Chemical Laboratory, opening exercises (note)..... 213
Kidney bean, proteids of 633, 703, 757
KILGORE, B. W. On the Estimation of Phosphoric Acid by Titration of the Yellow Precipitate, 765; The Determination of Phosphoric Acid by the Molybdate- Magnesia Method..... 793
KRUG, W. H. Some Characteristics of California Wines..... 579

LABORATORY devices 869
Laboratory Manual, of Physiology and Urine Analysis (book review), 874; for Beginners (book review)..... 879
Laboratory notes..... 65
LANGLEY, J. W. The Use of Electrolysis in Technical Chemical Processes 49

Lead-tin and lead-antimony alloys, commercial valuation of 541
LIGHTFOOT, THOMAS MONTGOMERY. A Study of the Chemical Behavior of Arsenopyrite 624
Lime, determination in quicklime 721
LINDSAY, W. B. See Storer, Frank H.
LINTON, LAURA A. On the Technical Analysis of Asphaltum 809
LIVERSIDGE, A. The Specific Gravities of Some Gem Stones 205
LONG, J. H. Observations on American Oil of Turpentine, 844; Laboratory Manual of Physiology and Urine Analysis (book review) 874
LUNGWITZ, E. See Schweitzer, H.
Lysimeter, apparatus for determining solubilities 715

MCELROY, K. P. Detection of Salicylic Acid in Food, 198; Contraction of Aqueous Solutions of Acetone 618
MCILHINEY, P. C. The Iodine Figure of Rosin, 56; A New Method of Analyzing Fats and Resins, 275; The Analysis of Varnishes, 344; Gantter's Process for Determining the Iodine Figure of Fats, 372; The Quantitative Separation of Rosin Oil from Mineral Oils, 385; A Method of Determining the Koettstorfer Figure of Dark-Colored Substances 408
MAGEE, W. H. See Dennis, L. M.
Magnesium, action on manganous salts, 822; reducing action of 833
Malt, analysis of 353, 559
Manganous salts, action of magnesium upon 822
MASON, W. P., and J. W. Bowman. Loss of Gold and Silver During Scorification Assay, 313; Note on the Test for Strychnine 824
MASON, W. P. Estimation of Chlorine in Water (note), 71; The Phenolsulphonic Acid Process for Nitrates in Water (note), 72; Expert Testimony, 273; The Boric Acid Works at Lardarelo, 538; Notes on the Hardening of Mortar, 733; The Quality of Water Supplies 772
Metallic reducing agents, contributions to our knowledge of 833
Midwinter Fair Congress at San Francisco, the 645
Milk, determination of albumen in 712
MILLER, EDMUND H. Succinimid 433
MILLER, JOHN A. The Analysis of Malt 353
Mineral Resources of the U. S. for 1893 (book review) 572
Mineral oil, separation from rosin oil 385
Molybdenum dioxide, action of silver salts upon 569
Molybdenum hexachloride, attempt to prepare 577
Molybdenum trioxide, action of phosphorus pentachloride upon 425
Molybdic acid, action of potassium chromate and bichromate upon 565
Morphine, fallacies of post-mortem tests for 799
Mortar, notes on the hardening of 733
MORY, A. V. H. See Noyes, W. A.
Muffle for incineration of sugar 151

NARCEINE, the iodides of 361
Nebraska Agricultural Report, 1893 (book review) 573
Nessler comparator 872
Nessler stand 872
NEUBAUER, HUGO. On the Determination of Phosphoric Acid as Magnesium Pyrophosphate 289
New Books 69, 142, 428, 502, 571, 644, 717, 789, 873
Nickel, determination in nickel-steel 96, 112
NIEHLS, W. An Improved Mercury Thermometer for High Temperatures, 396; A Scale of Hardness for Glass 406
Ninth General Meeting (announcement) 575
Nitrogen, assimilation of (note) 432

Nitrates, estimation in water by phenolsulphonic acid (note), 72; determination in potable water.....122, 193
Notes.....71, 213, 431, 645, 719, 992, 880
NOYES, ARTHUR A. A Detailed Course of Qualitative Analysis (book review)..... 503
NOYES, W. A., and E. D. Frohman. The Volumetric Determination of Phosphorus in Steel 553
NOYES, W. A., and W. M. Blinks. The Determination of Benzene in Illuminating Gas 697
NOYES, W. A. Quantitative Work for Beginners in Chemistry, 59; The Detection of Strychnine in an Exhumed Human Body, 108; The Post-Mortem Detection and Estimation of Strychnine (note)..... 720
NOYES, W. A., W. M. Blinks, and A. V. H. Mory. Oil-Gas..... 688

OFFICIAL agricultural chemists, Washington meeting of (note)..... 431
Oil cake, determination of moisture and oil in..... 114
Oil, determination in oil cake, 114; device for weighing (note)..... 882
Oil-gas..... 688
Oils and fats. Die Schmiermittel, etc. (book review), 69; separation of rosin oil from mineral oils, 385; Koettstorfer figure of dark-colored fats..... 408
Organic Compounds of Every-Day Life, etc., (book review)..... 502
OSBORNE, THOMAS B., and Clark L. Voorhees. Proteids of the Wheat Kernel 524; Proteids of Cottonseed 778
OSBORNE, THOMAS B. The Proteids of the Kidney Bean.....633, 703, 757
Oxygen, the Discovery of (book review)..... 718

PALLADIUM, double bromides of..... 465
Paper-Making, the Chemistry of (book review) 875
Patents..... 67
PARKER, CHAS. E. A Safety Attachment for Riders..... 764
PEASE, F. N. See Dudley, C. B.
PELLET, H. Determination of the Crystallizable Sugar in the Beet..... 266
PEMBERTON, H. On the Determination of Phosphoric Acid..... 278
PETER, ALFRED M. Changes in Official Methods of Soil and Ash Analysis (note).... 792
PHILLIPS, FRANCIS C. Note on a Form of Silver Obtained in the Reduction of the Sulphide by Hydrogen..... 700
Phosphoric acid, determination of, 278; note on Pemberton's method for determination of, as compared with official methods, 282; determination as magnesium pyrophosphate, 289;direct estimation of citrate soluble, 304; determination of, 462; estimation by titration of the yellow precipitate, 765; determination by the molybdate-magnesia method..... 793
Phosphorus, determination in steel, 217; determination by the volumetric method, 224; determination in iron, steel, and ores which contain arsenic, 231; notes and queries on Dudley's method for determination in steel, 234; condition of, in iron and steel, 477; volumetric determination in steel..... 553
Physical chemistry, achievements and aims of..... 516
Pipette, new automatic..... 643
Plant food, waste and conservation of 1
Portland cement, chemical and physical examination of 161, 283, 323, 374
Potash, sources of error in methods of determining, in fertilizers, etc..... 364
Potassium iodide, estimation of, in organic mixtures, 157; sold as U. S. P., quality of.. 678
PRESCOTT, A. B. Closing Address Before the World's Congress of Chemists..... 867
Presidential address by Dr. H. W. Wiley 1
PRIESTLEY, JOSEPH. The Discovery of Oxygen (book review)..... 718
PROCTER, H. R. On the Qualitative Determination of Tanning Materials..... 247
Proteids of wheat, 524; of cottonseed, 778; of the kidney bean.....633, 703, 757
PUPIN, M. I. Thermodynamics of Reversible Cycles, etc., (book review)..... 430
Pyrites, estimation of sulphur in..... 398
Pyroxylin, manufacture and uses.....487, 543

QUALITATIVE Analysis, by A. H. Elliott (book review), 429: by Arthur A. Noyes (book review).... 503
Qualitative and Volumetric Analysis (book review)..... 873
Quantitative work for beginners in chemistry, by W. A. Noyes..... 59
Quicklime, determination of CaO in..... 721
QUINAN, CLARENCE. Convenient Burette Clamp (note)..... 719

RICE, CHARLES. An Apparatus (Lysimeter) for Determining Solubilities..... 715
RICHARDS, JOSEPH W. The Commercial Valuation of Lead-Tin and Lead-Antimony Alloys..... 541
RICHARDSON, GEO. M. Laboratory Manual and Principles of Chemistry for Beginners (book review)..... 879
Riders, safety attachment for..... 764
ROBINSON, F. C. A Constant Level Apparatus..... 405
ROBINSON, N. Some Sources of Error in Our Methods of Determining Potash in Fertilizers and German Potash Salts..... 364
Rock analysis, a plea for greater completeness in chemical..... 90
Rosin, iodine figure of..... 56
Rosin oil, separation from mineral oils..... 385
Ross, B. B. The Direct Estimation of Citrate Soluble Phosphoric Acid, 304; Recent Work on the Sugars..... 549, 670
Ruthenium, nitrosochlorides of..... 388

SACCHAROMETER for sugar analysis..... 677
Salicylic acid, detection in food..... 198
San Francisco, midwinter fair congress..... 645
SARGENT, GEORGE W. See Smith, Edgar F.
SAUER, EWALD. A New Form of Air-Bath..... 31
SCHANCHE, H. G. Hydrogen Sulphide Generator..... 868
SCHEELE, CARL WILHELM. The Discovery of Oxygen (book review)..... 718
SCHEUCH, F. C. See Stone, W. E.
SCHWEITZER, H., and E. Lungwitz. A New Muffle for Incineration of Sugar..... 151
Select Methods in Chemical Analysis (book review)..... 789
Sewage Disposal at Worcester, Mass..... 682
SHINN, OWEN L. See Smith, Edgar F.
SHIMER, P. W. Note on the Determination of Silica in Blast-Furnace Slag..... 501
Silica, determination in blast-furnace slag..... 501
Silver, loss in scorification assay, 313; accuracy of commercial assay for..... 505
Silver obtained by the reduction of the sulphide by hydrogen, form of..... 700
Silver salts, action of molybdenum dioxide upon..... 569
SMITH, EDGAR F., and Daniel L. Wallace. Double Bromides of Palladium..... 465
SMITH, EDGAR F., and George W. Sargent. The Action of Phosphorus Pentachloride upon Molybdenum Trioxide..... 425
SMITH, EDGAR F., and Henry C. Burr. An Attempt to Prepare Molybdenum Hexachloride..... 577
SMITH, EDGAR F., and Henry E. Spencer. Electrolytic Separations..... 420
SMITH, EDGAR F., and Jos. G. Hibbs. The Action of Hydrochloric Acid upon Sodium Vanadate..... 578
SMITH, EDGAR F., and Owen L. Shinn. Action of Molybdenum Dioxide upon Silver Salts..... 569
SMITH, EDGAR F. Electrolytic Separations, 93; Electro-Chemical Analysis (book review), 574; See also Hibbs, Jos. G.
SNYDER, HARRY. Notes on the Grandeau Method for the Determination of Humus in Soils..... 210
Sodium acetate, estimation of, in organic mixtures..... 157
Sodium fluoride, volatility of..... 418
Sodium vanadate, action of hydrochloric acid upon..... 578

Soil and ash analysis, changes in official methods of (note)..... 792
Soils, chemical and physical investigation of..... 34
Solubilities, apparatus for determining..... 715
Solutions, dropping flask for standard..... 156
SPENCER, HENRY E. See Smith, Edgar F.
SQUIBB, EDWARD R. An Automatic Zero Burette..... 145
Standard solutions, dropping flask for..... 156
Starch, comparison of methods for the determination of..... 726
STEBBINS, JAMES H., JR. On the Estimation of Potassium Iodide and Sodium Acetate in the Presence of Complex Organic Mixtures..... 157
STILLMAN, THOMAS B. The Chemical and Physical Examination of Portland Cement.....161, 283, 323, 374
STONE, W. E. A Comparison of Methods for the Determination of Starch..... 726
STONE, W. E., and F. C. Scheuch. A Method for Determining Calcium Oxide in Quicklime..... 721
STORER, FRANK H., and William B. Lindsay. An Elementary Manual of Chemistry (book review)..... 644
Strontium and barium, occurrence in silicate rocks, 81; estimation of small amounts of..... 83
Strychnine, detection in an exhumed human body, 108; post-mortem detection and estimation of (note), 720; note on the test for..... 824
Succinimid..... 433
Sugar, determination of crystallizable, in the beet..... 266
Sugars, recent work on.....549, 670
Sulphur, estimation in pyrites..... 398
Sulphuretted hydrogen. See hydrogen sulphide.
Sulphuric acid, improvements in the manufacture of..... 498
Sulphur in pig-iron, standard solution of iodine for..... 112

TABLES from U. S. Pharmacopeia (book review)..... 430
Tanning materials, qualitative determination of..... 247
Tannin, the Tannins (book review)..... 428
Tariff, preliminary report of committee on..... 102
Thermodynamics of Reversible Cycles, etc., (book review)..... 430
Thermometer, improved mercury, for high temperatures..... 396
TIEMANN, FERD. See De Laire, G.
Titanium, separation from iron..... 427
TREVOR, J. E. The Achievements and Aims of Physical Chemistry..... 516
TRIMBLE, HENRY. The Tannins (book review)..... 428
Turpentine, observations on American..... 844

VANDERPOEL, FRANK. Dropping Flask for Standard Solutions..... 156
VAN SLYKE, L. L. The Determination of Albumen in Cow's Milk..... 712
Varnishes, analysis of..... 344
VENABLE, F. P. An Examination of the Chlorides of Zirconium, 469; A Short History of Chemistry (book review)..... 876
VERSON, E. Botrytis Bassiana and its Crystalline Products..... 860
VOLNEY, C. W. Apparatus for Fractional Distillation..... 160
VOORHEES, CLARK L. See Osborne, Thomas B.

WADMAN, W. E. Cream of Tartar Substitutes: Their Chemistry and Analysis 333
WALDBOTT, SIGMUND. On the Volatility of Borax, 410; On the Volatility of Sodium Fluoride..... 418
WALLACE, DANIEL L. See Smith, Edgar F.
WALLER, ELWYN. Laboratory Devices..... 869
Wash-bottle, compressed air..... 148
Waste of plant food..... 1
Water analysis, estimation of chlorine (note), 71; estimation of nitrates in (note), 72, 122, 193

Water-bath constant level 405
Water of crystallization of calcium bromide and iodide..... 681
Water supplies, quality of..... 772
WELLES, A. H. Patents of Interest to Chemists..... 67
WESTESSON, JOSEPH. Notes on Determination of Nickel in Steel 110
Wheat, proteids of 524
WILEY, H. W. The Waste and Conservation of Plant Food, (Presidential Address), 1; Correction, 432; The Chemical Midwinter Fair Congress at San Francisco, (note), 645; Assimilation of Free Nitrogen (note) 432
WILLARD, JULIUS T. An Introduction to the Organic Compounds of Every-Day Life (book review)..... 502
Wines, characteristics of California..... 597
WOLFBAUER, F. Method for the Determination of the Freezing-Point of Fatty Acids 665
WOLL, F. W. Recent Progress in the Analysis of Cattle Foods..... 174
Wool grease..... 535

ZIRCONIUM, examination of the chlorides of, 469; separation of, by sulphurous acid 475

Issued with October Number, 1894.

THE BROOKLYN MEETING.

AUGUST 15 AND 16, 1894.

THE Brooklyn meeting was a very interesting one. The attendance was large, the papers numerous and interesting, and the excursions and social features successful and enjoyable.

The meeting was opened in the Chemical Lecture Room of the Brooklyn Polytechnic Institute on Wednesday, August 15, at 10 A. M., by Dr. Wm. McMurtrie, Chairman of the Committee of Arrangements, who briefly stated what arrangements had been made, and welcomed the visiting chemists. After a brief response by President H. W. Wiley, the Secretary made some announcements and stated that 728 names were now on the roll of members, and that of these only thirty-eight had not paid dues for the current year.

Dr. Wm. H. Hale presented through the Secretary, on behalf of the street railway companies, 500 trolley tickets for the use of members, for which a vote of thanks was passed.

The following papers were then read and discussed:

Contributions to the Chemistry of Cerium.
L. M. DENNIS and W. H. MAGEE.

Utilization of Acid Sulphates, particularly the so-called Niter Cake of the Trade JOHN ENEQUIST.

Oxidation of Non-drying Oils by Air WALTER D. FIELD.

Oil-Gas W. A. NOYES.

Determination of Benzene in Illuminating Gas W. A. NOYES.

The Secretary announced that Dr. Wolcott Gibbs had been unanimously nominated by the Council for election to honorary membership in the society. Upon motion of Prof. C. E. Munroe, Dr. Gibbs was unanimously elected to honorary membership by a rising vote and the Secretary was directed to inform Dr. Gibbs of this action by telegraph.

The editor was called on for information about the JOURNAL and stated that considerably over 900 copies were now being sent out, only a few being exchanges. Probably 875 of these copies represent paid subscriptions, either of members or non-members. The number of subscribers who are not members is large and growing. The JOURNAL has been enlarged to seventy-two pages, and it has become necessary to reprint the January,

February, and March numbers, the first edition having been exhausted. A considerable amount of copy was now on hand and it would probably be necessary to still further enlarge the JOURNAL before the close of the year. Some further improvements were in contemplation but not yet ready for announcement. The greatest difficulty in the way of the Committee on Papers and Publications was in the lack of sufficient funds to print the material which came to the editor. He ventured to hope that members would bestir themselves in inducing proper persons to become members of the Society.

The President congratulated the members of the Society upon the good showing made. A charter for a Local Section had just been granted to the New Orleans chemists, and another section was in process of formation in San Francisco. With the present rate of increase the membership would doubtless exceed 1,000 before the close of the year. Chemistry has a great future in America. There is every reason to think that with proper effort we may have in this country the greatest chemical society the world has ever seen.

In the afternoon an excursion on the steamer "Blackbird" through the East river and adjacent parts of Long Island Sound had been arranged by the local committee. Stops were made at the Mineral Water Manufactory of Mr. Carl H. Schultz, 430–440 First Avenue, New York.

The party was met on the dock by Dr. Schultz and Dr. Hallock, who escorted them to the factory. After doing justice to a luncheon, served by Delmonico, the members were shown through the works by Dr. Schultz, Dr. Hallock, chemist, and Mr. Louis Waefelaer, mechanical engineer.

Established in 1862, these works have now grown to enormous proportions. The factory building is a substantial brick structure, four and five stories in height, covering half a city block. The factory is divided into nineteen departments:

Boiler rooms, engine rooms, siphon-testing department, gas-generating department, buffing department, siphon-filling department, bottle-filling department, pumping station, refrigerating department, water-purifying department, distilling department, cooling department, storage department, chemical department, foundry department, machine shop, electroplating department, carpenter shop, stables.

The carbon dioxide used in the water is generated in heavy lead-lined copper cylinders, from ground dolomite and sulphuric acid, after which it passes through a set of coolers, washers and purifiers to completely remove all impurities. It is stored in a gas-holder, from which it is

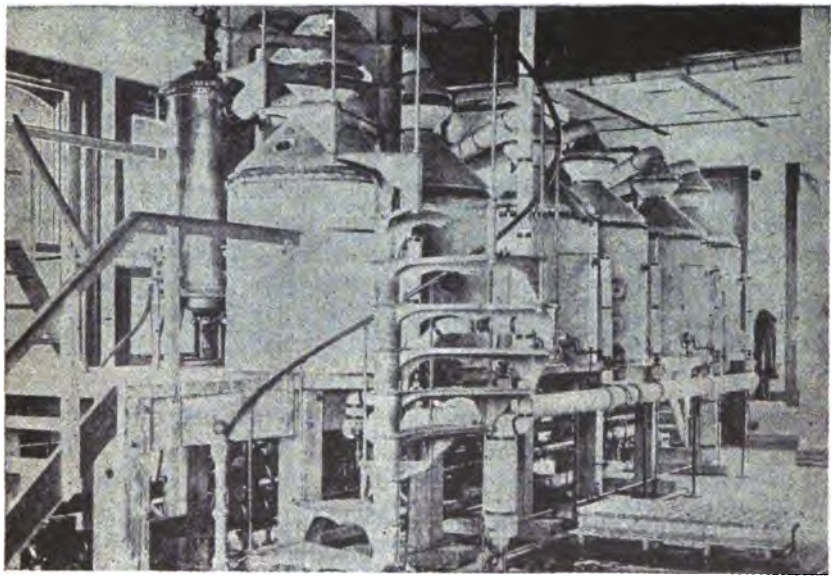
drawn for use in the siphon-filling machines, or compressed in large iron tanks to be used in charging the water in bottles or fountains.

In the building situated on First avenue, are placed the siphon-filling rooms. The solutions containing the numerous ingredients necessary for the production of a correct mineral water are first prepared from standard solutions in the laboratory, and sent over to the siphon-filling department and introduced into large marked vessels. These vessels are filled up to the mark with cold distilled water and thoroughly mixed with a stream of carbon dioxide. Two samples are taken, one from the top and the other from the bottom of the tank, and sent to the laboratory for examination. No siphons can be filled from a solution until it has been examined by the chemist and found to be correct.

The solution flows into a pail, and from this pail it is pumped into the machine. The pump takes the solution in on one side, and the gas in on the other; after compressing the gas into the water, the charged water is forced into a cylinder or reservoir on the top of the machine, from which it is conducted to the siphon.

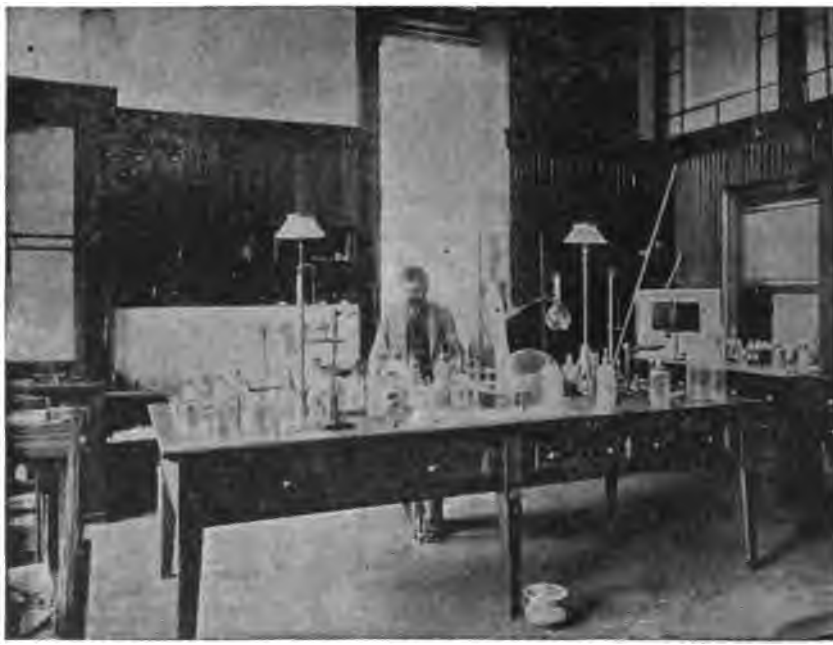
After many costly experiments Dr. Schultz found that the only way to obtain a pure and tasteless distilled water, was to thoroughly remove all impurities before distilling. In order to remove all suspended matter, the water is pumped through an ingenious filter invented and patented by his deceased son Carl H. Schultz, Jr. It consists of a large vessel suspended on trunnions which can be easily inverted, quickly washed out and afterwards sterilized with live steam, which not only thoroughly cleanses the filtering media, but destroys all organic growth, which has been the great objection to the use of filters. These filters are cleaned and sterilized every day. In the basement are also the boilers, refrigerating machine, cooling coils and hoisting machinery.

The croton water used is pumped in from the street mains and through



DISTILLING APPARATUS.

the sterilizing filter. Then it passes up-stairs through a set of heat exchangers, which are upright tin-lined copper cylinders containing a large number of one-inch pipes. Here it meets the hot distilled water coming down, thereby cooling the distilled water and heating up the filtered water. On the top floor the water is heated up as much as possible with exhaust steam from the ice machine, then boiled with live steam to drive off the volatile organic matter, the steam being drawn off with an exhaust fan and thrown away. After the removal of the volatile organic matter, the water flows down into the feed-boxes which are constructed to maintain a constant level of water in the stills. The stills, six in number, are arranged in three sets of two each. They are constructed of heavy copper, thoroughly tinned inside. They are about three feet in diameter and four feet in height, surmounted with a dome and separator to prevent any solid particles from being carried over with the steam. They are provided with water and steam gauges, two hand-



ANALYTICAL LABORATORY.

holes on each side for cleaning, and two glass peep-holes on opposite sides on the top. In front of one of the holes a gas-jet is kept burning, which furnishes light to the inside of the still.

The condensation of the steam for distilled water, takes place in tall vertical cylinders, containing a large number of small pipes, through which the cooling water is pumped. Only one condenser is required for two stills. The large amount of cooling effect is obtained indirectly from river water, and to guard against contamination which would result from the river water getting into the distilled water, only croton water

is run through the condensers, and this hot water cooled down for use again by pumping it through a series of coils, over which a stream of river water is kept constantly running.

The distillation is accomplished by steam supplied from two large steam boilers. This steam, which is still very hot when it leaves the still, is conducted to the top floor and used for preheating the water before distillation, thereby utilizing all the heat.

The hot distilled water after leaving the condensers passes down through a set of heat exchangers where it is cooled down as much as possible by the filtered croton water, and then through a second set where it is cooled down to about 40° F. by cold water from the refrigerating machine. It is then stored cold in large covered tanks provided with cotton-plugged vents to prevent any contamination from the air. All the apparatus is constructed of heavily tinned copper, the conducting pipes are made of block-tin and all the valves are silver-plated to guard against any possible metallic contamination.

On the second floor are the laboratories. They consist of two large rooms where the solutions are prepared, and two smaller rooms for analytical work. One of these rooms is especially fitted up for water analysis, and bacteriological work; besides these, there is a small dark room for spectrum analysis and photographic investigation.

The walls are hard finished and painted, and all around is a white pine wainscoting of narrow boards about eight feet high, leaving a space of about three inches from the wall; in this space the water and gas pipes are placed so as not to be seen. The wainscoting is built in sections so any section can be removed, in case it is necessary to get at the pipes for repairs. In the upper part of the partitions are large ground-glass fanlights which can be opened when extra ventilation is required. The doors have large panels of chipped glass with the names of the different departments cut in. The hood and around the sinks are lined with white tile, giving it a neat appearance, and can easily be kept clean. The front is entirely taken up with large windows furnishing plenty of north light and ample ventilation even in the warmest weather.

The laboratory is well-equipped with all the necessary apparatus, for Dr. Hallock is one of the few fortunate chemists whose employer is generous enough to give him *carte-blanche*.

The luncheon served by Delmonico was unique and deserves special mention. The only appropriate adjective that can adequately describe it is, superb. A pleasant feature was the figures of chemical apparatus with appropriate mottoes designed by Dr. Hallock. One of these represented two retorts with crossed necks and the inscription: "Treat with an excess of C_2H_5OH," another a picture of a liter flask inscribed, "Fill up to the holding mark."

In returning thanks Dr. Wiley remarked that his idea of the term "mineral waters" had been much enlarged. At the morning session he had suggested that he was not accustomed to lunch on mineral water. That remark he now wished to withdraw entirely. Mr. Schultz responded.

Returning to the steamer the party proceeded to Willet's

Point, where they were welcomed by Colonel King and staff. The visitors were shown an immense electro-magnet, made by using one of the old Rodman guns as a core, and three torpedoes were exploded and photographed. The party then inspected the Museum of Engineering Models and reviewed the parade.

The officers, twenty-five in number, are West Point graduates. There are 425 enlisted men also stationed here. The officers follow the course laid down in the school schedule, while the men are drilled and instructed in the various duties of engineer troops.

THURSDAY, AUGUST 16.

Papers read and discussed:

Note on the Hardening of Mortar.....WILLIAM P. MASON.

Note on the Test for Strychnine.....WILLIAM P. MASON.

The Quality of Water Supplies.....WILLIAM P. MASON.

The Bacteriology of the Soil as Affected by Depth, Character and Use.....LUCIUS PITKIN.

Report on Abbreviations of the Names of Metric Terms Used by Chemists.....WM. H. SEAMAN.

Some Points in Making Molybdate of Ammonia Solutions for Phosphorus Determinations.....CHARLES B. DUDLEY.

Ucuhuba Fat.....JOSEPH F. GEISLER.

[This paper was read by title in the absence of the author.]

A New and Rapid Method of Estimating the Total Proteids in Milk.....E. H. BARTLEY.

At this point the session was adjourned in order that the members might be free to attend the meeting of Section C., of the American Association for the Advancement of Science, to listen to the address by Vice-President T. H. Norton.

At the adjourned session the following papers were read:

Inspection of Cotton for Use in Gun-Cotton Manufacture.
CHAS. E. MUNROE.

Ferric Acid and the Ferrates.....C. A. O. ROSELL.

After a vote of thanks to Dr. E. R. Squibb and Sons, Edward Smith and Co., Carl H. Schultz, Dr. A. P. Hallock, Col. W. H. King, Willet's Point, Mr. Wolf, Disinfecting Plant, Riker's Island, The Long Island Brewery, The Hygienic Ice Co., The Standard Oil Co., The Bergen Point Chemical Works, The Fogarty Gas Co., The Balbach Smelting and Refining Co.,

Feigenspan's Brewery, and the Trustees and Faculty of the Brooklyn Polytechnic Institute, the meeting adjourned.

THURSDAY AFTERNOON.

Some forty or fifty of the chemists visited the Vacuum brewing and the ice-making plants. At the brewing works they were shown through vault after vault full of immense casks of the "Lager," were given a lunch and shown the apparatus for cooling the beer and for forcing carbonic acid gas through it after the fermentation, since by the vacuum method not enough of the gas was formed in it.

At the ice works they were shown the whole process in so far as it could be easily seen: the pumps, the cans in which the water was frozen, with the various stages of the operation which requires about three and a half days for completion, the method of taking the ice cakes out of the cans, etc.

At various times during the meetings, parties of chemists visited the works of Dr. E. R. Squibb and Sons and Edward Smith and Co.

The factory of E. R. Squibb and Sons, for the manufacture of acetic acid and acetates, is a large plant at the foot of Gold street, on the East river water front of Brooklyn. The plant is divided into wood yard on the water front and factory proper in the rear. First were shown the machinery and appliances for cutting up the wood into small billets. Then the loading of this cut wood into iron retorts or cars which run on elevated tracks by means of winches. By these tracks the cars are run into and out of air-bath cells for the distillation of the wood. Each car or retort holds about 2.8 cords of wood, and each oven has twelve cells for as many cars, and the firing and draft flues pass under the floors of the cells, so that the combustion of fuel and its products do not get contact with the retorts or cars of wood. Each retort or car has an eduction pipe which passes through the rear wall of the cell and is connected with a large Liebig condenser. The distillation is conducted at temperatures below 204° C. (400° F.) of the air-bath and the process requires about seven days for each retort. The first day yields water only. Then comes very weak crude acetic acid, and the strength slowly and steadily increases up to about twenty-five per cent. This crude, smoky acid contains but little tar, and when saturated with soda-ash the salt is dried and heated until nearly anhydrous. It is then decomposed with two equivalents of sulphuric acid in a still of peculiar construction with a mechanical stirrer, and yields very strong acetic acid of good quality. This acid is then rectified from bronze stills through glass or silver condensers, yielding the various strengths of fine acid. The commercial grades of acid of different strengths for use in the arts, are made in large stills of ordinary construction from commercial calcium acetate of the markets: decomposed with sulfuric or hydrochloric acid.

The wood after distillation is allowed to cool in the retorts and is then dumped and put up in bags of fifty pounds each, and sold to railroads, steamboats, fire departments, etc., as a kindling material for coal, being

itself an almost perfect fuel, easily lighted, and efficient in very small quantity.

This factory is under the management of Mr. Charles F. Squibb, who was always ready to show it to any of the members of the Society sufficiently interested to accept the invitation of the firm.

The pharmaceutical laboratory was shown to those who visited it during the meeting, chiefly by Dr. E. H. Squibb, who now relieves his father in the management of that part of the business of the firm. It is a large building of five stories, built around a central court yard, and the general plan is to manufacture in the upper stories, store and fill in the next lower, and finish and stock in the next lower, while the ground floor is used for offices, shipping, storage of material, etc. The basement contains the boilers, engines, mills, pumps, drying hoods, etc. The ether apparatus occupies a detached section of the building three stories high, and is fire-proof like many of the other parts. The building is supplied throughout with good apparatus and fixtures too complicated and varied to be comprehended in a short visit, and both apparatus and workmen were clean and orderly. Everything was freely shown and all questions were freely and frankly answered in accordance with the long-established policy of E. R. Squibb and the present policy of E. R. Squibb and Sons.

At the factory of Edward Smith and Co. were seen: First, supplies of raw material; all the commonly known kinds of copal resins, both fossil and recent; also dammar and shellac; linseed oil both raw and prepared for use; refined turpentine having a constant boiling-point, and the still used in redistilling it; the utensils and plant employed in varnish-making, with the operations actually going on; the testing of the finished goods; the most recent improvements in mills, etc., for grinding pigments in varnish and japan; the technical chemical laboratory; and in general, the methods in common use for the management of the manufacturing part of the varnish business. There were to be seen a very large collection of samples of resins and oils, and the kettle in which was made the first batch of varnish ever made in America, besides some old Dutch varnish kettles more than forty years old and still in use.

On Saturday, 18th, the party visited the Standard Oil Works and the Bergen Point Chemical Works at Bayonne, and the Balbach Smelting and Refining Works and Feigenspan's brewery at Newark. This was a joint excursion with Section C. of the American Association for the Advancement of Science. The following account written by one of the party, is abbreviated from one of the Brooklyn daily papers.

The sail down New York Bay was a charming one. The temperature was just right, the atmosphere was clear and the refreshing breeze invigorating.

The first works inspected were the refineries of the Standard Oil Company at Bayonne. The chemists were given every opportunity to inspect the plant, and the processes were carefully explained by the manager, Mr. Van Winkle. The oil comes in through two six-inch pipes, and is started from the pumps under a pressure of about twelve hundred pounds. From the receiving tanks the oil is pumped into a number of stills, each having a capacity of 600 barrels. The products obtained from these stills are a light naphtha, heavy naphtha, white oil, distillate and slops in the order given. The white oil is sold for illuminating purposes,

and the distillate is refined by treatment with acids before it is used for illumination.

It takes three days to run off a "charge" from one of these stills, and it is then thoroughly cleaned before being charged again.

The tarry residue from these stills is treated for lubricating oil and paraffin being pressed through canvas at a temperature of 60° to 65° F., and that which runs out being again subjected to pressure at a much lower temperature.

The distillate from the stills is treated with sulphuric acid, then with steam in an agitator, then with soda and washed to fit it for the market.

After the sludge acid is removed from the tarry product a porous, nearly pure carbon is left which is sold, much of it being used to make the carbon pencils for electric arc lights.

The next visit was to the Bergen Point Chemical Works near by. Here sulphuric acid is made from iron pyrites, and the sludge acid from the Standard Oil Company's Works is refined.

At the Balbach Works, lead ore carrying silver, gold and other metals, is received by steamer from Mexico, and, after treatment, the refined products are shipped to the European market.

The ore is roasted in a reverberatory furnace to remove first the copper and then the antimony as dross.

After these are removed it is put into the softening furnace where other impurities are driven off, and it is then treated by the Parke process for separating the silver and gold from the lead.

The silver, gold, zinc, and some of the lead rise up to the surface and are skimmed off together to be separated from one another by further processes, that which remains being lead, carrying a little zinc and other impurities. This is refined and the pure lead is then ready for the market.

The skimmings from the Parke process are first heated in a crucible of plumbago to drive off the zinc, which comes off as a vapor. This vapor is condensed to liquid zinc, which is run into moulds and allowed to cool.

Silver, lead and gold are then passed on to the crucible by dumping the latter. After cooling, the mass is transferred to a cupel, where it is again melted and a current of air passing over the molten surface changes the lead to litharge which floats upon the surface and is drawn off, leaving the pure silver and gold.

To separate the silver from the gold the combined metals are treated with hot sulphuric acid, which dissolves the silver but does not attack the gold. The silver sulphate thus formed is transferred to a vat in which are placed thin plates of copper. By this means the silver is deposited in the pure metallic state and the copper goes into solution, and is sold to be used in making crystals of copper sulphate.

Many other processes of interest were shown, such as methods of sampling and assaying, charging the blast-furnace, treating the various slags and dross.

The last visit of the day was that to the Feigenspan brewery in Newark, which proved a most interesting part of the day's excursion.

The Board of Directors have granted a charter for a Local Section in New Orleans and vicinity.

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